100 AMPERE-HOUR NICKEL-CADMIUM

BATTERY CELLS OF IMPROVED DESIGN

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by

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for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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100 AMPERE-HOUR NICKEL-CADMIUM

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SUMMARY

100 ampere-hour sealed nickel-cadmium battery cells with novel design features were developed. These design features, notably extension of the current collector tab to the full width of the battery plate, and location of the cell terminals on opposite ends, resulted in a substantial reduction of internal impedance, and improved electrical performance which should improve the thermal performance characteristics.

Five laboratory prototype cells were fabricated in accordance with the Preliminary Cell Design and tested to verify compliance with the Cell Requirements. The Preliminary Design was modified to reduce cell weight by 2% and to increase cell capacity by 6%. Forty-four cells were fabricated in accordance with the Final Cell Design, twelve incorporated the Adhydrode auxiliary electrode as an end-of-charge signaling device. All cells were tested and met the Acceptance Test Criteria. Five of these cells were subjected to a Characterization Test Program, a series of charge-discharge tests over a wide range of rates (C/10 to C) and temperatures (32°F to 110°F).

INTRODUCTION

Conceptual design studies of power systems for long term manned orbital laboratories have established the need for several large capacity secondary batteries on each spacecraft to compliment the prime power source. These studies have recommended that the basic component of each battery be a sealed, nickel-cadmium cell of approximately 100 ampere-hour capacity. The selection of a nickel-cadmium cell was based on a demonstrated longer cycle life and a rapid recharge capability required in low earth orbits.

Under Contract No. NAS 1-4289 for NASA/Langley Research Center, Gulton Industries designed, fabricated and tested 100 ampere-hour hermetically sealed nickel-cadmium cells. The units developed demonstrated a capability to provide up to 120% of rated capacity when discharged at the C rate to 1.0 volt per cell, and up to 135% of rated capacity when discharged at the C/10 rate to 1.0 volt per cell. This cell was essentially a scale-up of the hermetically sealed prismatic cell presently in use in

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unmanned orbital spacecraft. Testing of these cells indicated that, although a reasonable specific energy density was achieved at the required high discharge rates, they had some deficiencies. The discharge voltage was low, the charge voltage was high, and heat generation during discharge appeared excessive. Additional testing also revealed that harmful voltage and temperature gradients could exist in the battery plates as a result of current non-uniformities. The observed internal impedance was 1.5 milli-ohms, which was only slightly less than that of the much smaller 20 Ah cell. To obtain the same relative voltage characteristics, the impedance of the 100 Ah cell should be one-fifth (1/5) that of a 20 Ah cell. In addition, to maintain the same level of I^2R heating, the effective impedance of the 100 Ah cell should be about one-twenty-fifth (1/25) that of the 20 Ah cell.

The objective of this program was to improve the design of the 100 Ah cell to eliminate the voltage and thermal gradients. To affect a substantial reduction in internal impedance, and to overcome some of the observed de-ficiencies, the cell was redesigned to incorporate design features gener-ated at LRC. This new design approach has been termed the "balanced geometry" design.

Figure 1 shows the basic difference between the conventional cell and the "balanced geometry" design.

The basic difference is the use of a full width plate current collector tab and the location of the terminals at opposite ends of the cell, as com-pared to a narrow plate current collector tab and having the terminals on the same end, as in the conventional cell. The anticipated benefits of the new cell design over the conventional approach were a major reduction in internal impedance and greatly improved electrical and thermal character-istics. The specific tasks and the resultant findings are detailed in the following sections.
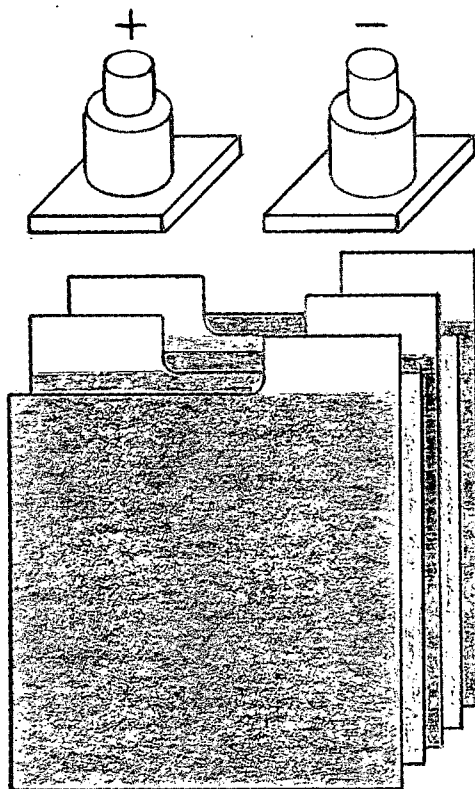
CONVENTIONAL
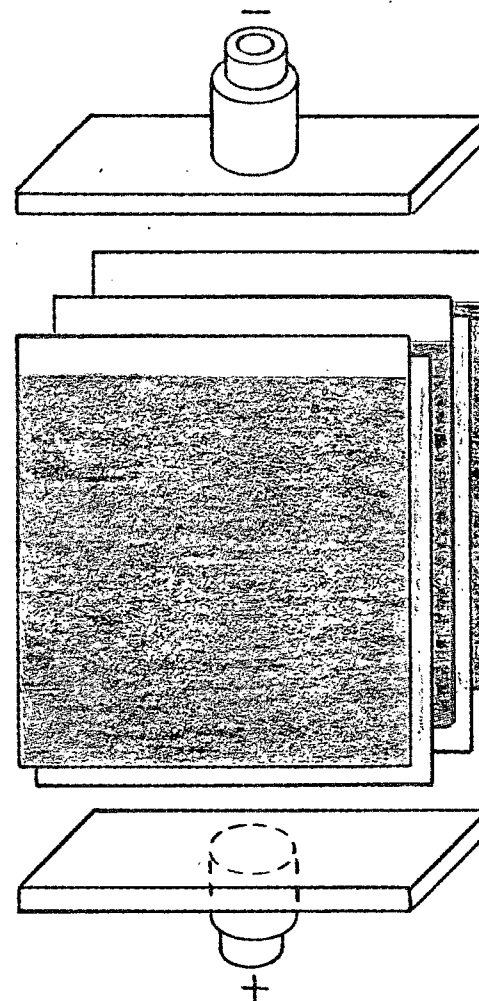
BALANCED GEOMETRY

FIGURE 1.   PRISMATIC NICKEL-CADMIUM BATTERY
CELL DESIGN

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5-3059

DESIGN CONSIDERATIONS

The following requirements were considered in the design of the cell:

Cell Requirements

Electrical Requirements.

a. The specific energy density of the cell, when discharged at 100 amperes to 1.00 volt at 70°F, shall be 15 watt-hours per pound or greater.

b. Cell capacity, when discharged at 100 amperes to 1.00 volt at any temperature from 50°F to 90°F, shall be 110 Ah or greater.

c. Cell capacity, when discharged at 10 amperes to 1.00 V at 70°F, shall be 120 Ah or greater.

d. Cell voltage at the midpoint of a 100 ampere discharge, at 70°F, shall be 1.20 V or greater.

e. Internal cell pressure after 24 hours of overcharging at 10 amperes, and at 70°F, shall not exceed 45 PSIA.

f. The charge retention of a fully charged cell after 7 days of storage at 110°F shall be greater than 80% of the initial ampere-hour capacity, measured at the 25 ampere discharge rate.

Mechanical Requirements.

a. Cell weight shall not exceed 9.0 lbs.

b. As a goal, cell dimensions shall be as follows:

Case height, less terminals	7.3 in.
Case width	7.3 in.
Case thickness	1.4 in.

c. Cell case material shall be 304L stainless steel, not to exceed 0.032" in thickness.

d. The cell case shall be designed to withstand a minimum of 150 PSI of internal pressure with the large cell surfaces restrained.

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e. Cell terminals of opposing polarity are to be located on opposite ends of the cell. Each terminal shall be insulated from the cell case with a ceramic-to-metal seal which incorporates a strain relief collar between the ceramic and metal. All silver containing braze joints shall be coated to prevent silver migration.

f. The electrode support plaques shall be high purity nickel. The current collector tab shall be an integral part of the support plaque and shall extend the full width of the plate.

g. The cells shall have a maximum leak rate of 10^{-7} standard cc of helium per second.

Preliminary Cell Design

A thorough analysis was made of each cell component to achieve a design which would maximize cycle life and cell performance, and minimize size and weight. In selecting materials for the cell components, properties such as density, conductivity, strength, compatibility, workability, cost and availability were carefully considered.

For the cell case and cover, AISI 304L stainless steel was the material of choice. To contain the maximum operating cell pressures, the minimum wall thickness was calculated to be 0.025". However, the requirement that an internal pressure of 50 psi shall not cause a permanent deformation with the wide faces restrained, dictated that the wall thickness be increased to 0.031". For the terminal, which was required to carry up to 100 amperes, copper and silver were considered because of their high conductivity. Silver, however, was rejected because of its high cost, and because its higher conductivity was offset by its higher density. For the terminal base and for the comb bars, nickel 200 was selected (over several grades of steel) because of its higher conductivity and its compatibility with the system. The insulator was a high alumina (90% min.) ceramic, and the stress relief members were 42% nickel-iron alloy to match the thermal expansion characteristics of the ceramic. The seal assembly is shown in Figure 2.

Concurrently with the design studies, electrochemical investigations were carried out to aid our design effort. A positive plate, cut to the dimensions shown in Figure 3, had insulated nickel wire spot welded to three locations on the tab (A, B, C) and to nine (1 to 9) locations of the plate. The nine contacts on the plate were made by scraping some sinter off to expose the nickel substrate for making contact. The plate with the welded leads was inserted into a non-woven nylon separator bag. Two negative plates of identical size were placed on either side of the bagged electrode and the whole assembly placed in a KOH filled container. While the electrode assembly was charged and discharged at the two-hour rate, IR drops between each of the three points in the tab and each of the nine locations were measured in all possible combinations. These results, shown in Figure 3, indicated that there were no gradients in the horizontal direction in the plate. The observed gradient was in the vertical direction; it was uniform across the plate, and with the terminals located on opposite ends, was expected to offset that in the adjacent plate.

The preliminary cell design which had evolved from these initial studies was as follows:
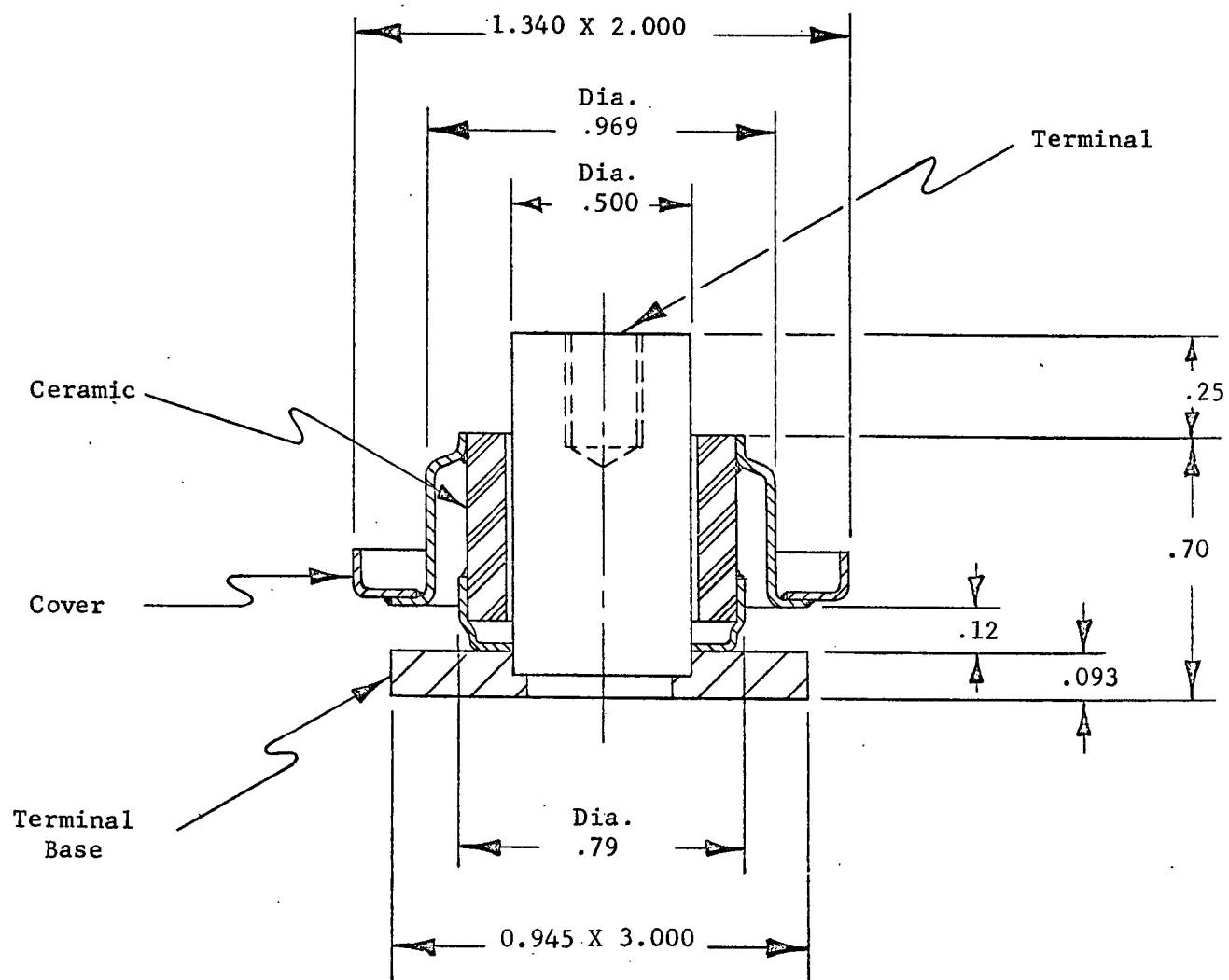
FIGURE 2.   CERAMIC-TO-METAL SEAL USED IN THE
100 AH CELL

	A		B		C	
A	0.4		A	0.4		A	0.4
B	0.4		B	0.5		B	0.3
C	0.5		C	0.4		C	0.4
	①			②			③
A	1.0		A	0.8		A	0.9
B	0.8		B	0.8		B	0.9
C	0.9		C	0.8		C	0.8
	④			⑤			⑥
A	1.4		A	1.4		A	1.4
B	1.6		B	1.3		B	1.2
C	1.3		C	1.3		C	1.3
	⑦			⑧			⑨
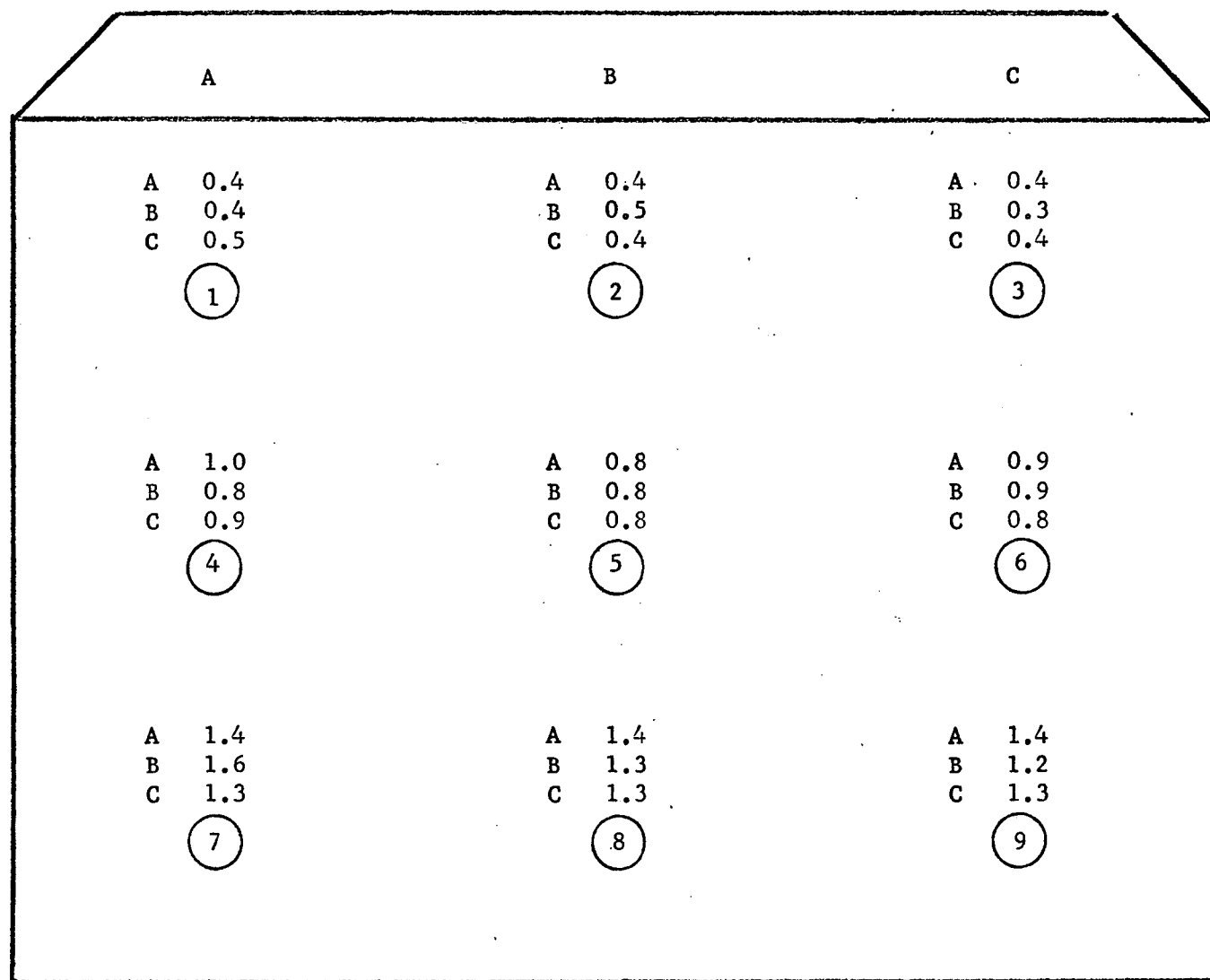
FIGURE 3.   VOLTAGE DROP, IN mV, BETWEEN TAB AND PLATE AREAS

IN VO-100HS PLATE WHILE CHARGING AND DISCHARGING AT C/2 RATE

Electrode Design

a. Electrode support - Nickel 200, 0.003" thick, perforated.

b. Plaque porosity - 70% min., 75% max., 72% nominal.

c. Plate dimension - 7.000" x 5.905" x 0.031", excluding plate tab.

d. Plate area and capacity - 41.3 sq. in., 7.4 Ah per plate, min.

Cell Design

a. Design capacity - 111 ampere-hours at the one-hour rate.

b. Cell case material - 304L stainless steel, 0.031" thick.

c. Ceramic-to-metal seal -- cross-sectional view as shown in Fig. 2.

d. Weight - 8.93 lbs.

e. Size - Case height - 7.7"
         Case width - 7.3"
         Thickness   - 1.4"

f. Plate count - 15 positives and 16 negatives.

g. Separator - non-woven nylon

h. Electrolyte - 34% KOH solution, low carbonate content.

Cell Impedance. - The cell impedance was calculated from the geometry and conductivity of the component parts, arranged in a series-parallel network as shown in Appendix I. The results of these calculations were as follows:

Terminal Assemblies (2)	95×10^{-6} ohms
Contribution from plate support	29×10^{-6} ohms
Separator-electrolyte layer	165×10^{-6} ohms
Total Cell Impedance	289×10^{-6} ohms

Calculated Heat Generation . - A major objective in the design of the cell was to minimize heat generation on discharge. When discharging a nickel-cadmium cell, heat is generated by IR and polarization losses (Joule heating), and by the exothermic cell reactions.

At the one-hour discharge rate (100 A), the I^2R heat contribution will be:

$$(100 \text{ A})^2 \times 2.9 \times 10^{-4} \text{ ohms} = 2.9 \text{ watts}$$

or 2.9 watt-hours for a 60 minute discharge. The resulting rise in cell temperature, assuming no heat loss to the surroundings, will be:

$$\frac{2.9 \text{ watt-hrs} \times 3.413 \text{ BTU/watt-hr}}{0.25 \text{ BTU/lb} - °F^* \times 8.93 \text{ lbs}} = 4.4°F$$

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* Brooman, E. W., "An Annotated Bibliography of the Thermal Properties of Primary & Secondary Cells", Technical Report No. AFAPL-TR-70-34 (June 1970) Wright-Patterson Air Force Base Contract No. F33615-69-C-1537.

The heat generated by the reaction exotherm is associated with the entropy changes, the difference between the heat of reaction (ΔH) and the free energy of reaction (ΔG). For the nickel-cadmium system, $\Delta H - \Delta G$ is 3.5 kcal/equiv* which will result in a cell temperature rise of

$$\frac{111 \text{ Ah} \times 3.5 \text{ kcal/equiv} \times 3.968 \text{ BTU/kcal}}{26.8 \text{ Ah/equiv} \times 0.25 \text{ BTU/lb} - °F \times 8.93 \text{ lbs}} = 25.8°F$$

Total cell temperature rise then, after a one-hour discharge at 100 A, will be 30°F, the rise being due primarily to the reaction exotherm, with only a small fraction being due to resistance losses.

Measured values on four cells at the end of a 100 A discharge to 1.0 V were 13°F to 14°F as shown below.

Final T	ΔT	Discharge Time
92°F	14°F	61 min.
96°F	14°F	66 min.
94°F	13°F	64 min.
93°F	13°F	68.5 min.

These measurements were made with a thermistor in intimate contact with the cell case (304L stainless steel) at the center of the wide face. During these tests, the cells were restrained with 8-3/4" x 7-7/8" x 5/16" steel plates, one against each of the two wide faces. If one calculates the expected temperature rise taking into account the added heat capacity of the restraining plates, the resulting values are 2°F due to I^2R heating and 11.6°F due to the discharge reactions. These values are in very close agreement with the observed findings.

PROTOTYPE CELL FABRICATION AND TESTING

Five (5) laboratory prototype cells were fabricated in accordance with the Preliminary Cell Design. These cells were tested to verify compliance with the program objectives and requirements, and to determine what design modifications, if any, are needed to further improve cell performance characteristics.

In the design and fabrication of the prototype cells, every attempt was made to approximate the final cell design so that the thermal and electrical behavior observed during evaluation would be indicative of what might be expected of the end product. The one exception to this approach was the terminal seal. The prototype cells used "O" ring seals, whereas the final cell used ceramic-to-metal seals. This difference was not deemed significant.

Four of the five cells were fabricated with the normal plate count (15 positives and 16 negatives) and one cell was fabricated with an extra set of battery plates (16 positives and 17 negatives). The external

* "Alkaline Storage Batteries" by S.U. Falk and A. J. Salkind, John Wiley & Sons, New York, Chapter 7.

dimensions of the five cells were identical. They were:

    7.70" high (less terminals)
    7.30" wide
    1.40" thick
    8.24" height (including terminals)

The first of these cells was used to determine the proper electrolyte content. After assembly, the dry cell was weighed, 250 cc of 34% KOH was added, and the cell was charged and discharged to check voltage, capacity and overcharge pressure. Following the first cycle, 15 cc and 10 cc incremental quantities of electrolyte were added to the cell. Each electrolyte addition was followed by charge-discharge testing with the following results:

Cycle No.	Volume of KOH Added	Discharge Time 1.0 V At C Rate
1	250 cc	50 min.
2	265 cc	47.5 min.
3	265 cc	47 min.
4	275 cc	60 min.
5	285 cc	60.3 min.
6-11	285 cc	57-60.5 min.
12	300 cc	66.3 min.

On cycles 6 to 11, the charge rate was varied from C/10 for 16 hrs. to C/2 for about 2.5 hrs., when the voltage showed a tendency to rise more sharply. End of charge pressure, checked when charging at C/10 for 16 hrs., reached a maximum of 9 psig on the 12th cycle.

The electrolyte quantity added was 300 cc for the 31-plate cells and 320 cc for the 33-plate cells.

The five (5) cells were subjected to the following Evaluation Test Program to verify compliance with the Cell Requirements, and to determine what modifications, if any, are required in the design:

a. Weight determination
b. Cell voltage after a 24 hour charge at C/10 (10A) at 70°F.
c. Cell pressure after a 24 hour charge at C/10 (10A) at 70°F.
d. Ampere-hour capacity at the C rate (100A) discharge at 50°F, 70°F, and 90°F.
e. Ampere-hour capacity at the C/10 rate discharge at 70°F.
f. Midpoint voltage at the C rate discharge.
g. Charge retention after a 7 day stand at 110°F.

Excepting the weight determination, all tests were performed in a circulating constant temperature oil bath (Aminco Model #4-8605), where the temperature was maintained within ± 1°F of the desired setting. Thermocouples were attached to two of the five cells (Nos. 3 and 5), at three different locations (one at the center of the wide face, one at the center of the narrow face, and one at the positive terminal), as shown in Figure 4, to check for any temperature difference between the cell and the oil bath. These measurements indicated that the temperature of the cell was at all times in equilibrium with that of the oil bath, as illustrated by the data in Table I.
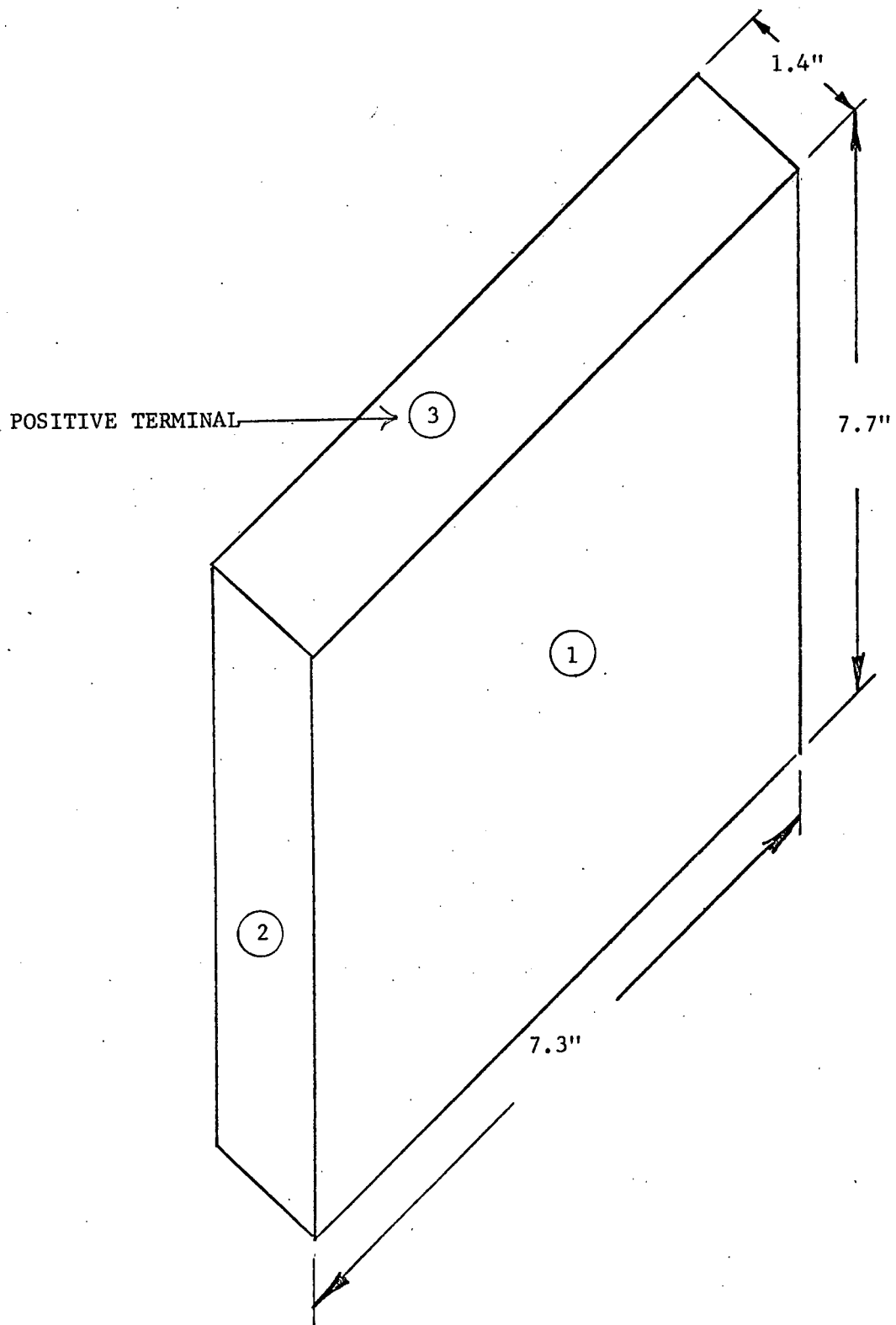
POSITIVE TERMINAL ——————→ ③

①

②

1.4"

7.7"

7.3"

FIGURE 4.   VO-100 CELL OUTLINE DRAWING
SHOWING LOCATION OF THERMO-
COUPLES FOR MEASURING CELL
TEMPERATURE

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The five cells were connected in series while charging and dis-
charging. A regulated constant current power supply was used to charge
and discharge the cells at a constant current, regulated to better than
± 1%. The prototype cell evaluation test results are summarized in
Table II. Typical data are shown in Figures 5 through 10.

Figure 5 shows voltage versus time at the 10 ampere charge rate,
at 70°F. Maximum cell voltage, 1.46 V, was reached at 13 hours. There-
after, it dropped and stabilized for the balance of the 24 hour period.
End of charge pressure stabilized at 15 psig.

TABLE I. - CELL TEMPERATURE AT THE END OF 100 AMPERE DISCHARGE

THERMOCOUPLE NO. *	THERMOCOUPLE READING, °F	BATH TEMPERATURE, °F
3-1	70	70
3-2	70	70
3-3	70	70
5-1	70	70
5-2	70	70
5-3	70	70
3-1	90	90
3-2	90	90
3-3	90	90
5-1	90	90
5-2	90	90
5-3	90	90

* The first digit denotes cell number; the second digit the
thermocouple location as illustrated in Figure 4.

TABLE II. - SUMMARY OF PROTOTYPE CELL EVALUATION TEST RESULTS

	PROTOTYPE CELL NUMBER				
	1	2	3	4	5
Voltage after 24 hr. C/10 (10A) Charge at 70°F..	1.445	1.45	1.445	1.445	1.43
Pressure after 24 hr. C/10 (10A) Charge at 70°F, psig.................................	15	6	4	17	30
C/10 Rate Capacity at 70°F, Ah..........	113	112	114	111	118
C rate capacity at 70°F Ah..............	108	103	107	107	113
Discharge Voltage at Midpoint (of C rate discharge)........................	1.23	1.22	1.22	1.22	1.23
C rate capacity at 50°F, Ah.............	103	102	100	100	107
C rate capacity at 90°F, Ah.............	110	105	108	103	113
Cell weight dry, lbs.....................	8.20	8.20	8.25	8.21	8.60
Cell weight wet, lbs.....................	9.07	9.07	9.14	9.10	9.54
Watt-hrs/lb, C rate, 70°F...............	14.7	13.9	14.5	14.4	14.5
Watt-hrs/lb, C/10 rate, 70°F............	15.7	15.5	15.7	15.3	15.6
Charge Retention - Ah capacity after 7 day stand in 110°F oil bath, 25A discharge rate to 1.0 V..........	96	89	99	95	96
Plate Count:					
No. of positives......................	15	15	15	15	16
No. of negatives......................	16	16	16	16	17

PROTOTYPE CELL #1

FIGURE 5.   10 AMPERE CHARGE AT 70°F

PROTOTYPE CELL #1

FIGURE 6.   10 AMPERE DISCHARGE AT 70°F

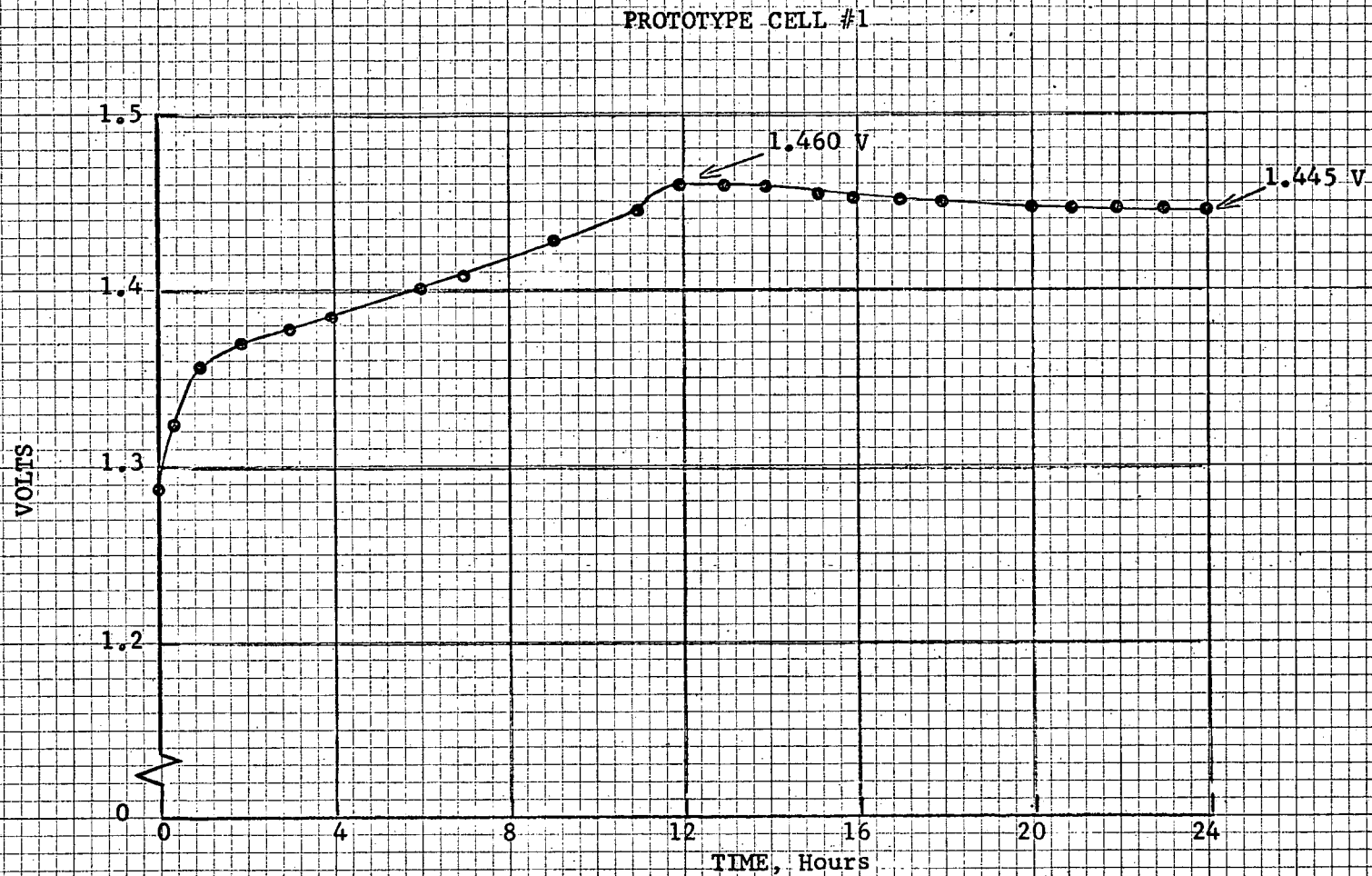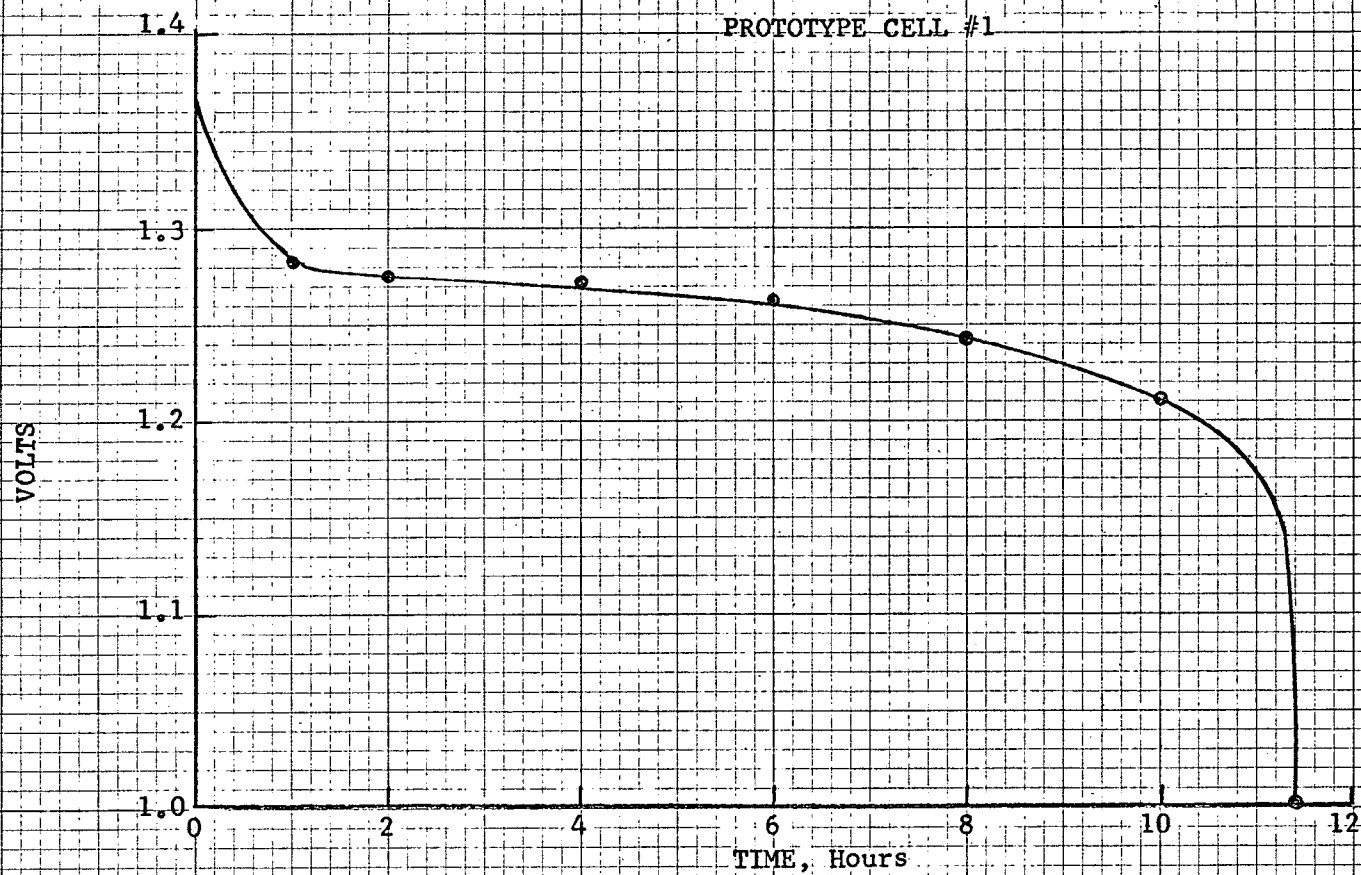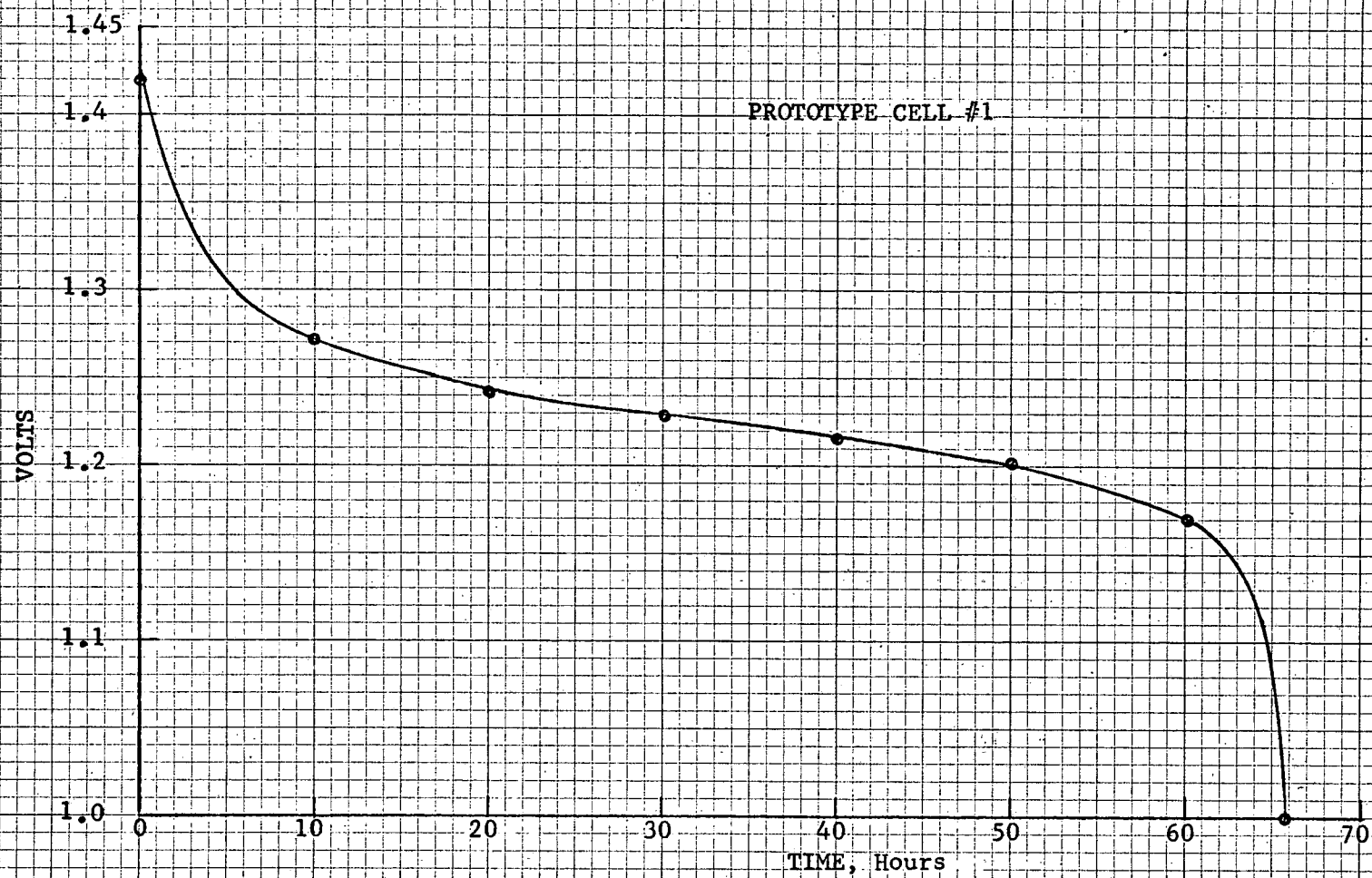PROTOTYPE CELL #1

FIGURE 7.   100 AMPERE DISCHARGE AT 70°F
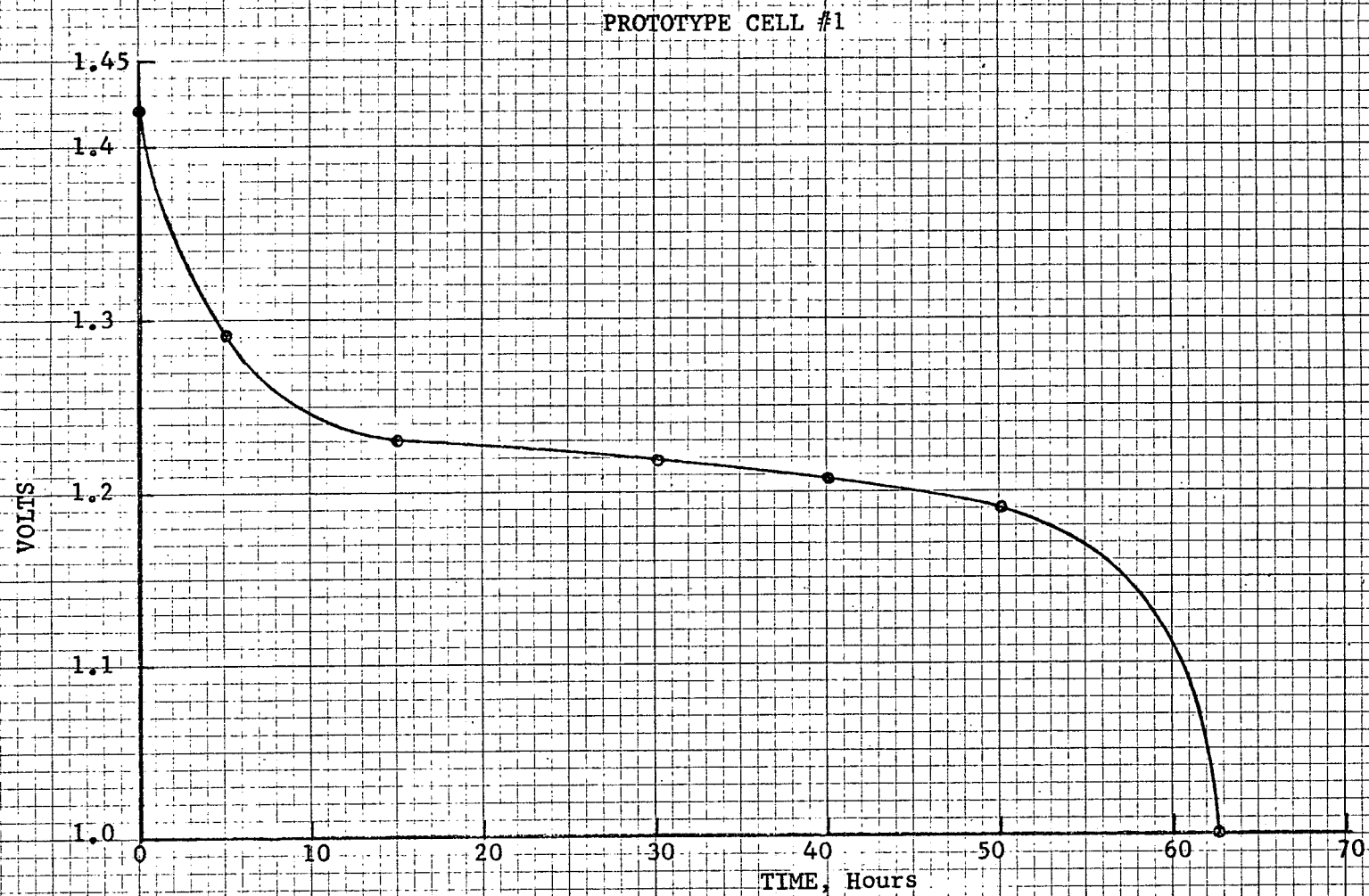
FIGURE 8.   100 AMPERE DISCHARGE AT 50°F

FIGURE 9.   100 AMPERE DISCHARGE AT 90°F
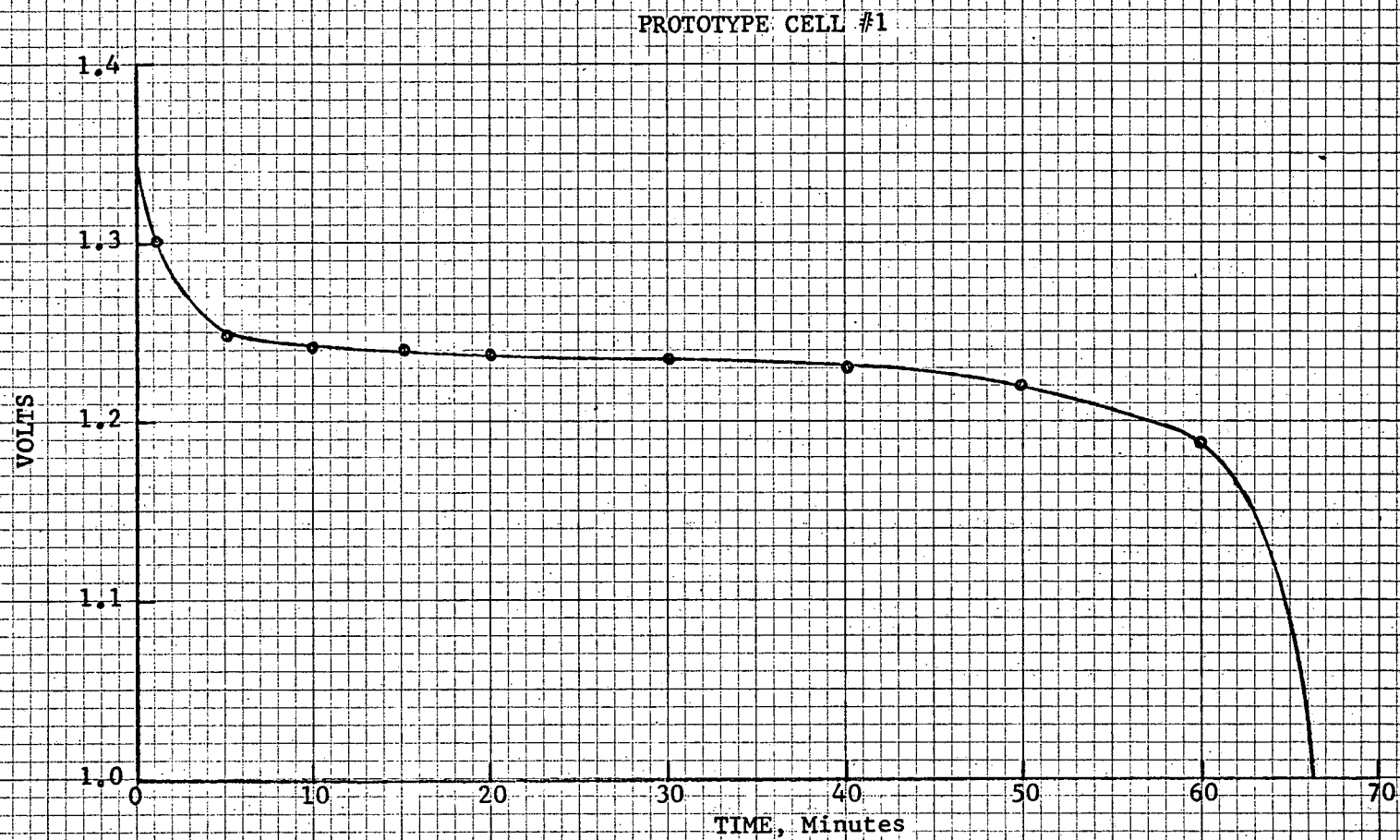
PROTOTYPE CELL #1

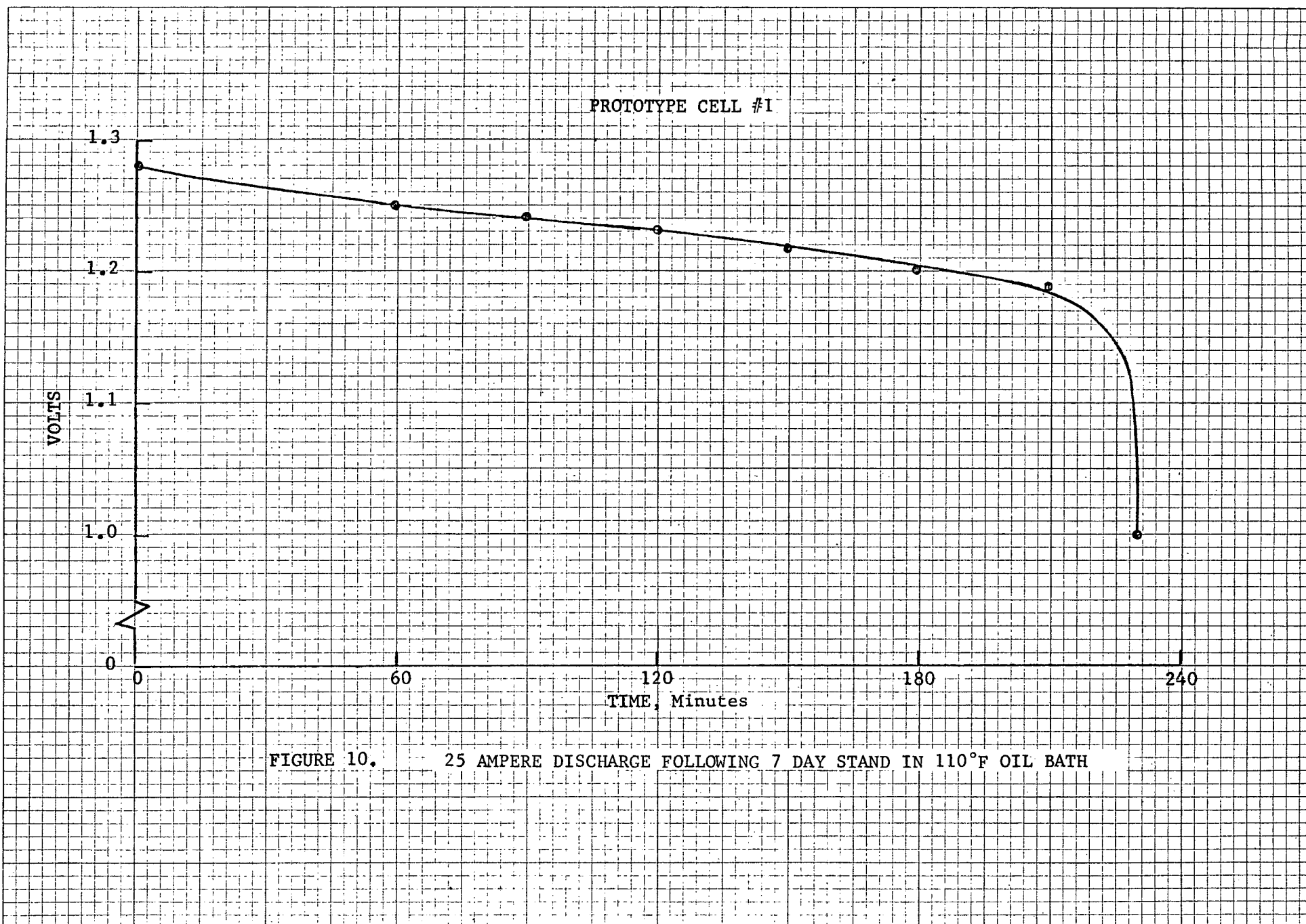FIGURE 10.   25 AMPERE DISCHARGE FOLLOWING 7 DAY STAND IN 110°F OIL BATH

Figure 6 shows voltage versus time during a 10 ampere discharge at 70°F. Figures 7, 8, and 9 show similar data during 100 ampere discharges at 70°F, 50°F, and 90°F respectively. The midpoint voltages exceeded 1.20 volts at each of the above temperatures. Figure 10 shows that the cells retained more than 80% of their capacity following a 7 day stand in a 110°F oil bath.

These results indicated that the cell design was sound, and that the Cell Requirements were substantially met, excepting cell weight which was slightly above the specified 9.0 lbs. max., and cell capacity was slightly below the required 110 Ah and 120 Ah at 100 ampere and 10 ampere rates, respectively.

FINAL CELL DESIGN

To effect a reduction in cell weight and an increase in cell capacity without adversely affecting cell performance characteristics, the following modifications were made in the Preliminary Design:

a. The amount of active material in the cell was increased by increasing plate thickness from 0.031" to 0.033".

b. The thickness of the comb bars was reduced from 0.125" to 0.093". The width of the comb bars, on the edge, was reduced from 0.18" to 0.090".

c. The width of the terminal base was reduced from 1.125" to 0.945", to correspond with the modified comb bar dimensions. The thickness of the terminal base was reduced from 0.125" to 0.093".

d. The cell case height was reduced from 7.70" to 7.60".

e. The electrolyte volume was increased from 300 cc to 310 cc to compensate for the increased plate thickness.

These design modifications, along with replacement of the "O" ring seals with ceramic seals, was calculated to reduce cell weight by approximately 0.15 lbs. and to increase cell capacity by 6% to meet the weight, capacity and energy density requirements of the cell. These design modifications, as shown in the following section, did, in fact, reduce cell weight below 9.0 lbs. and increased cell capacity to 110 Ah at the one-hour discharge rate.

An outline drawing and the internal construction of the final cell design are shown in Figures 11 and 12.

.31 MAX.

8.78   8.19   7.60

7.30

1.40
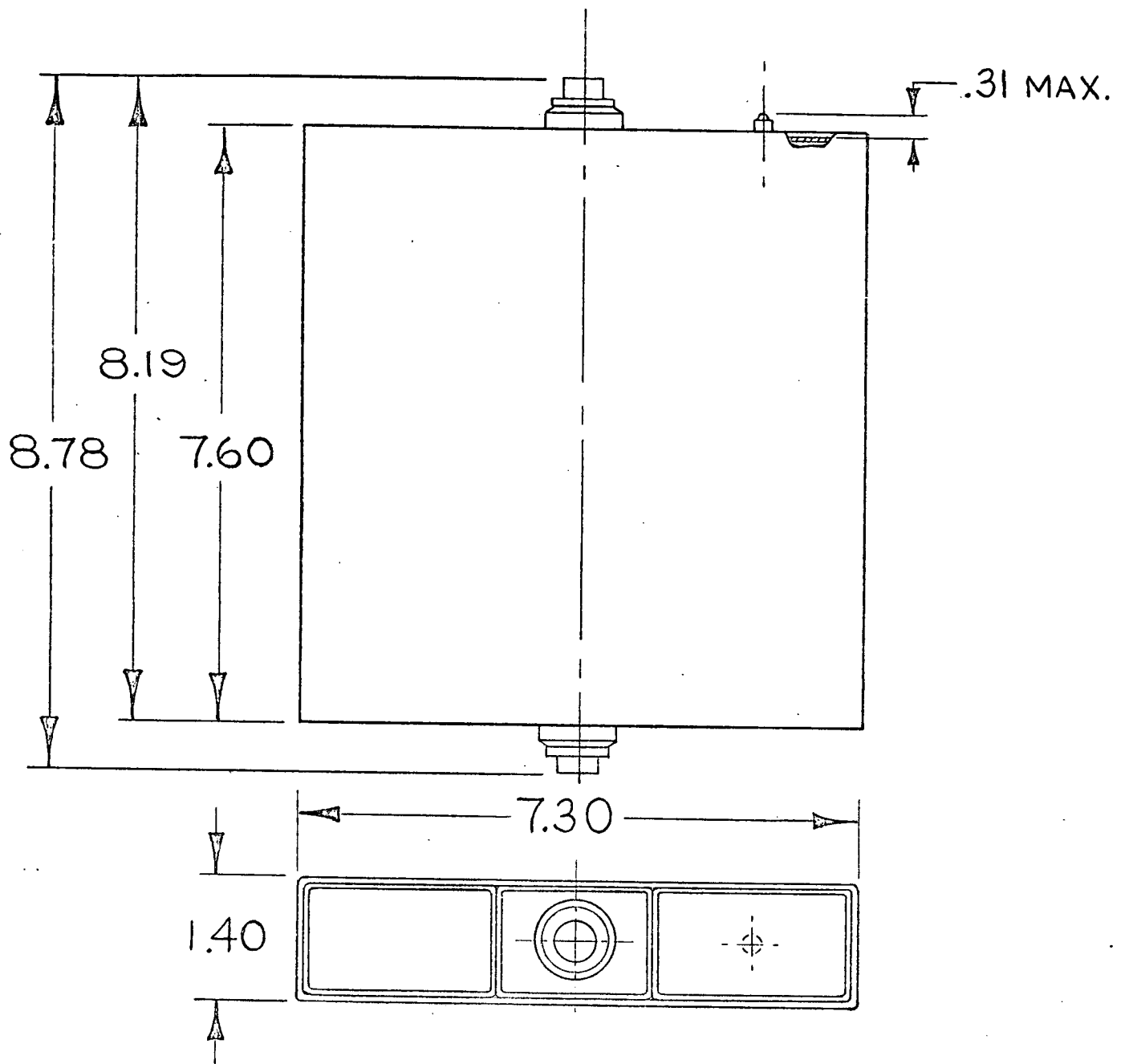
OUTLINE DRAWING
100 AH CELL

FIGURE 11.

POS. TERM.

TERM. BASE

LINER

COMB BARS

NEGATIVE PLATE

POSITIVE PLATE

SEPARATOR

NEGATIVE TERM.
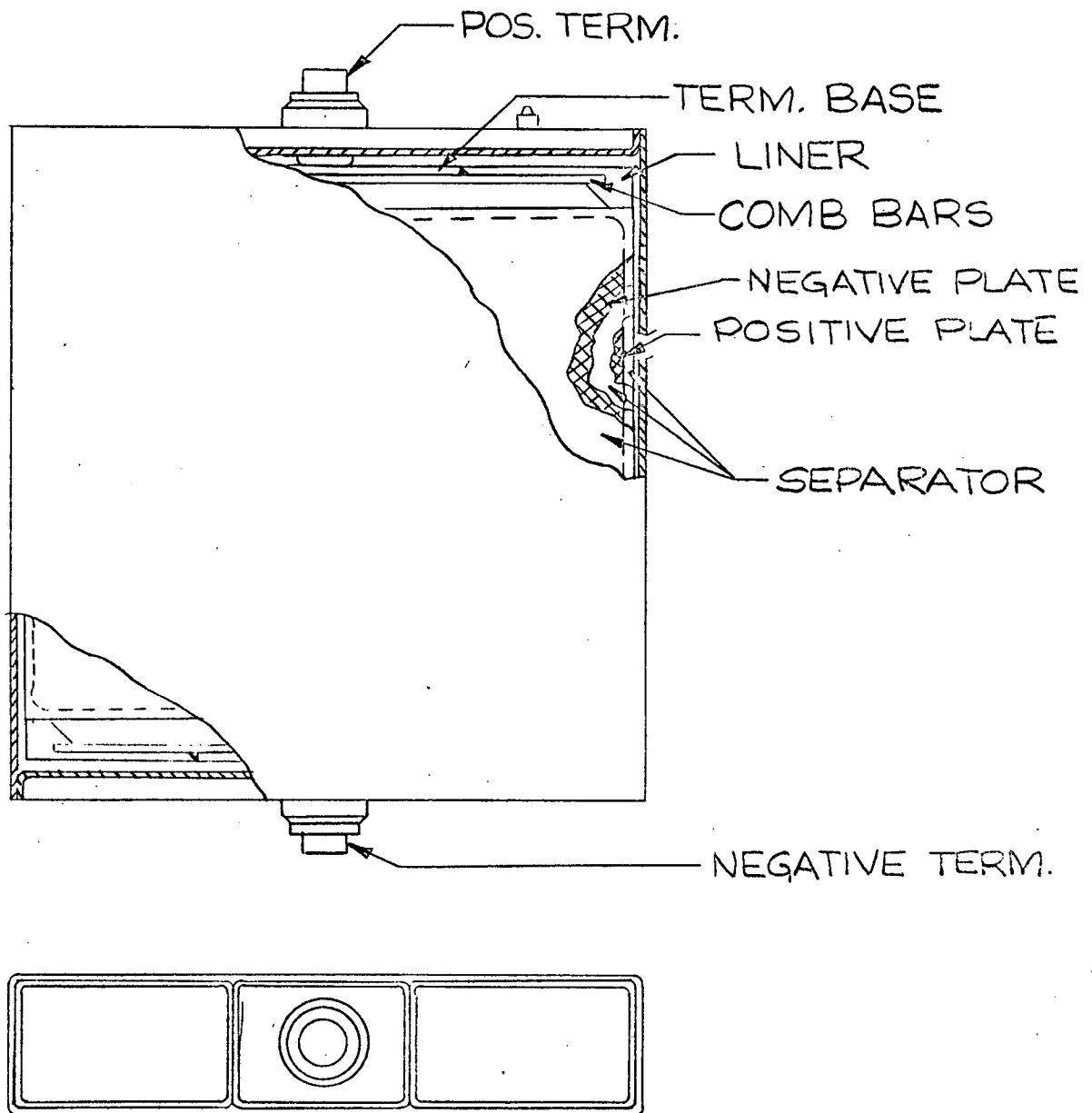
INTERNAL CONSTRUCTION
100 AH CELL

FIGURE 12

FABRICATION AND ACCEPTANCE TESTING

Forty-four (44) cells were fabricated in accordance with the approved Final Cell Design. Twelve of the cells were fabricated with the Adhydrode[R] auxiliary electrode as an end-of-charge signaling device. In addition, three of the twelve cells were fabricated with 14 positives and 15 negatives, one pair less than the normal plate count. However, so as not to alter the plate compression in the electrode stack (all cell cases had the identical internal and external dimensions), the normal plate count (31 plates) was used except that one positive and one negative plate were bagged individually and left disconnected from the plate stack. The extra plates were placed on one end of the plate stack so as not to interfere with the normal operation of the cell. The Adhydrode, of the same dimensions as the battery plate (7.00" x 5.906") was bagged and located adjacent to the outermost negative plate. It was internally welded to the steel case. Since both terminals were isolated, the cell case served as a third terminal.

Following mechanical assembly, the cells were activated by the addition of 310 cc of electrolyte. Each cell was then subjected to the following Acceptance Test Procedure:

a. Weight determination.

b. Overcharge voltage and pressure following 24 hours of over-charging at C/10.

c. Capacity at the 100 ampere rate following ten (10) charge-discharge cycles.

d. Leak rate of cells.

3. Internal electrical leakage test.

All tests were performed at room ambient. Weight determinations were made before and after the addition of electrolyte. The double weighing also served as a check on the electrolyte quantity added to each cell. The weight differences ranged from 408 gms to 414 gms, with the majority being 411 and 412 gms.

Overcharge voltage and pressure were measured following 36 hours of charging at 11 amperes. This procedure assumed 12 hours of charging and 24 hours of overcharging. Voltage and pressure were monitored and the 36 hour readings were stabilized values. Maximum acceptable pressure was 45 psia. Required overcharge voltage was 1.38-1.40 V.

Following the 36 hour charging, the cells were placed on automatic cycling. Each cycle consisted of a 30 minute discharge at 50 amperes, followed by 90 minutes charging at 20 amperes. Following the tenth charge cycle, the cells were discharged at 100 amperes to 1.0 V per cell. Required capacity was 66 minutes. Required midpoint voltage was 1.20 V or greater.

The leak rate of each cell case was measured on a Helium Mass Spectrometer prior to activation with electrolyte. The sensitivity of the instrument was 10^{-7} standard cc of He per second. In addition, while the cells were on overcharge, all welded joints were sprayed with a 1.0% solution of phenolphthalein for any evidence of leakage. At the conclusion of the Acceptance Testing, all cells were backfilled with a 5% helium-95% oxygen mixture and rechecked on the Helium Mass Spectrometer. No evidence of leakage was detected by any of these tests.

Internal electrical leakage was tested by shorting each cell for 16 hours following a discharge. The cells were then charged for 5 minutes at 10 amperes, and allowed to stand on open circuit for 24 hours. The open circuit voltage was measured after a 24 hour stand. The required OCV was 1.20 V.

The Acceptance Test Results are summarized in Table III. The results indicate that the cell weight variation was less than 2% (4001 to 4070) among the cells without the Adhydrode. All cells met the 9.0 lbs. maximum (4082 gms) weight requirement. The Adhydrode cells, because of the extra plate, were somewhat heavier, the heaviest one, #47AX, being 9.02 lbs.

Overcharge voltage was 1.38 V ± 0.02 V, while overcharge pressures ranged from 10 psia to 30 psia.

Cell capacities to 1.0 V ranged from 66 to 74 minutes at the 100 ampere discharge rate for the cells with the 31 plate count, excepting Cell #23, which yielded 64 minutes. Cells with the lower plate count (47AX, 48AX, and 49AX) were expected to yield approximately 6.5% less capacity than the others.

The open circuit voltage following the short test is an indication of internal electrical leakage. Only those cells which had readings of 1.19 or higher were selected for delivery, assuming they met all other requirements. However, it was felt that any cell which read 1.10 V or higher would be satisfactory for characterization testing, since no prolonged charged stand was included in these latter tests.

TABLE III. - SUMMARY OF ACCEPTANCE TESTS

CELL NO.	CELL WT. (gms)	V C/10 Chg.	PSIA C/10 Chg.	CAPACITY (Min.)	MIDPOINT V	V ON SHORT TEST
1	4008	1.40	10	74	1.22	1.17
2	4029	1.41	11.5	73	1.22	0.58
3	4046	1.41	24	73	1.22	1.14
4	4057	1.41	13.5	73	1.21	1.23
5	4023	1.39	13.5	69	1.19	1.20
6	4011	1.40	15	70	1.20	1.19
7	4008	1.39	15	70	1.19	1.23
8	4008	1.39	12.5	71	1.20	1.22
9	4001	1.40	15	70	1.19	1.22
10	4017	1.39	24	67	1.19	1.21
11	4009	1.40	16	68	1.20	1.20
12	4031	1.39	15	69	1.20	1.22
13	4021	1.39	10.5	67	1.20	1.08
14	4015	1.41	17	67	1.20	1.20
15	4029	1.40	16	69	1.20	1.21
16	4041	1.40	21	67	1.20	1.21
17	4049	1.38	16	66	1.19	1.20
18	4048	1.38	12.5	68	1.19	1.22
19	4032	1.38	15	67	1.19	1.22
20	4026	1.41	18	70	1.21	1.23
21	4061	1.40	12.5	66	1.205	1.11
22	4042	1.40	24	69	1.21	1.24
23	4055	1.40	23	64	1.20	1.25
24	4040	1.39	27	66	1.20	1.24
25	4044	1.39	10	69	1.205	1.22
26	4035	1.39	17	68	1.20	1.24
27	4041	1.39	20	69	1.21	1.23
28	4021	1.39	20	67	1.205	1.24
29	4041	1.41	21	67	1.20	1.24
33	4051	1.40	18	70	1.22	1.26
35A	4088	1.40	26	72	1.22	1.26
38A	4083	1.39	26	70	1.21	1.23
39A	4073	1.39	21	71	1.21	1.24
40A	4073	1.40	22	73	1.22	1.23
41A	4070	1.41	10	73	1.19	1.25
42A	4084	1.41	17	68	1.21	1.19
43A	4074	1.42	13	68	1.21	1.24
47AX	4093	1.40	27	69	1.23	1.24
48AX	4083	1.38	24	63	1.21	1.26
49AX	4054	1.39	20	65	1.22	1.16
50	4060	1.40	21	66	1.19	1.23
52	4046	1.39	30	66	1.22	1.24
53	4070	1.40	21	65	1.22	1.23
55A	4074	1.38	26	65	1.22	1.23
56A	4087	1.39	20	66	1.22	1.23

Notes: V and PSIA denote voltage and pressure following 36 hours of charging at 11 A. Midpoint V is voltage at 33 minutes into discharge at 100 A. A suffix following cell number denotes Adhydrode cell. AX denotes cell with lower plate count.

The negative-to-positive ratio was measured on a sample cell. Here the cell was flooded with electrolyte, charged at 20 amperes for 16 hours at room ambient, and discharged at 50 amperes. A reference electrode with a DVM was used to determine the limiting electrode. Cell capacity to +1.0 V was 137 Ah, to -0.5 V, 187 Ah. The positive electrode was the limiting one, and the negative-to-positive ratio was 1.36:1.

The integrity of the cell case was tested by restraining the wide faces of the cell, pressurizing the cell case, and measuring the displacement and permanent deformation along the narrow cell faces. This cell case was pressurized with oxygen, the increase in cell width was measured, the pressure was relieved, and the width was remeasured. This was done with two cells with the following results:

PRESSURE (PSIG)	DISPLACEMENT	PERMANENT DEFORMATION
CELL #54A		
22	0.0015"	0
30	0.003 "	0
42	0.0055"	0
60	0.009 "	0.001 "
78	0.012 "	0.002 "
90	0.0145"	0.003 "
102	0.017 "	0.0042"
CELL #44A		
15	0	0
20	0.0004"	0
30	0.001 "	0
40	0.002 "	0
50	0.003 "	0
75	0.008 "	0.001 "
81	0.0095"	0.0012"
90	0.0117"	0.0019"
100	0.0144"	0.0033"

The first sign of permanent deformation occurred at 60 psig or more. At lower pressures, the cell case returned to its original dimensions when the pressure was relieved. These measurements were made on one side of the cell, using a platform dial gauge, and the values shown above represent 50% of the total dimensional changes, assuming the cells behaved symmetrically.

CHARACTERIZATION TESTING

Five (5) cells which completed the Acceptance Test Procedure were selected for the Characterization Tests. The five selected for this purpose were cells #1, #3, #13, #21, and #25.

The Characterization Test Program was as follows:

Voltage And Pressure Vs. Time At
50°F, 70°F and 90°F

Cell voltage and pressure were measured as a function of ampere-hour input and ampere-hour output at the following charge and discharge rates:

Charge Rate	Discharge Rate
10 amperes	10 amperes
10 amperes	25 amperes
10 amperes	50 amperes
10 amperes	100 amperes
25 amperes	50 amperes
25 amperes	100 amperes
50 amperes	25 amperes
50 amperes	100 amperes
100 amperes	100 amperes

Each of the above charge-discharge tests was performed at 50°F, 70°F, and 90°F.

Voltage And Pressure Vs. Time At 32°F

Cell voltage and pressure were measured as a function of ampere-hour input and ampere-hour output at 32°F, using the following charge and discharge rates:

Charge Rate	Discharge Rate
10 amperes	50 amperes
10 amperes	100 amperes
25 amperes	50 amperes
25 amperes	100 amperes

Voltage And Pressure Vs. Time At 110°F

Cell voltage and pressure were measured as a function of ampere-hour input and ampere-hour output at 110°F using the following charge and discharge rates:

Charge Rate	Discharge Rate
25 amperes	50 amperes
25 amperes	100 amperes
50 amperes	50 amperes
50 amperes	100 amperes

Charge Efficiency

The coulombic charge efficiency of the test cells was determined by measuring the minimum amount of charge required to obtain cell capacity. These determinations were made at 50°F, 70°F, and 90°F, using charge rates of 10 amperes and 50 amperes. The discharge rate was maintained at 25 amperes.

All the above tests were performed in a circulating constant temperature oil bath, with the bath temperature maintained within ± 1°F· of the desired setting. The five test cells were connected in series while completely immersed in the oil. A knife switch arrangement permitted individual cells to be switched out of the circuit and bypassed when desired. Charging and discharging was done using a constant current power supply with a 150 ampere current capability, regulated to better than ± 1%.. The current was read on a Weston Model 931 millivolt meter with a 100 ampere, 50 mV shunt.

Test Results

The characterization test results are summarized in Table IV and typical data are plotted in Figures 13 to 22.

The plotted data indicate that the load sensitivity of these cells was relatively small. At 50°F and 70°F, the difference in discharge voltages between 10 ampere and 100 ampere rates was approximately 50 mV or less. At 90°F and 110°F these differences were even smaller. At 110°F, the 50 ampere and 100 ampere curves are nearly superimposed.

At 50°F and 70°F, the cells were efficiently recharged at all rates, and the discharge rate appeared to influence cell capacity to a greater extent than the charging rate. For example, at 70°F at the 100 ampere discharge rate, the average capacities of the 5 cells were 116 Ah and 118 Ah, following 10 ampere and 100 ampere charge rates respectively.

On the other hand, the average cell capacities at the 25 ampere and 100 ampere discharge rates were 121 Ah and 115 Ah respectively. Similarly, at 50°F, average cell capacities at the 25 ampere discharge rates were 121 Ah and 119 Ah following 10 ampere and 50 ampere charge rates respectively. At the 100 ampere discharge rates, average cell capacities were 116 Ah and 115 Ah for 25 ampere and 50 ampere charge rates respectively. However, average cell capacities were 120 Ah and 114 Ah at the 25 ampere and 100 ampere discharge rates, respectively.

Coulombic charging efficiencies (ratio of Ah output to Ah input) are shown in Table V. At 50°F, both the 10 ampere and 50 ampere charge rates were about equally effective (tests #14 and #13). Similarly, at 70°F, both the 10 ampere and 50 ampere charge rates were effective.

At 90°F, however, the cells did not deliver their rated capacity when charged at 10 A even for 16 hours. To obtain cell capacity, charge rates of 25 A or greater had to be used. Evidently, temperature had a greater effect on charge acceptance (oxygen gassing) than the charging rate because the cell capacities at 90°F were lower than at 70°F and 50°F over the full range of charge and discharge rates. This observation becomes more apparent when examining the 110°F data. At this temperature, there was a significant difference between the C/2 and C/4 charge rates. The higher charge rate yielded substantially more capacity at both the 50 A and 100 A discharge rates. However, even the C/2 charge rate for 2-1/2 hours did not recharge the cells fully. The poor charge acceptance at higher temperature must be attributable to a lowering of the oxygen overvoltage with increasing temperature. At a higher cell temperature, a greater fraction of the charging current goes into generating oxygen at the positive electrode, resulting in a poorer charging efficiency. Consequently, both the charging rate and the ampere-hour input need to be increased to obtain effective recharging.

At 32°F, the electrical performance characteristics of these cells was very poor. As the end of charge was approached, cell voltages rose to high levels where hydrogen evolution occurred. Consequently, charging was done with a voltage limit of 1.50 V. This voltage limitation prevented a full charge and, therefore, the cells failed to deliver their rated capacity. It was suspected that this poor behavior was due to a high carbonate in the cells. Following the 32°F tests, the bath temperature was raised to 70°F and two charge-discharge tests (#43 and #44) were run with satisfactory results. Following the 70°F tests, electrolyte samples were taken from the cells and analyzed for carbonate. These analyses showed 100-175 gms of potassium carbonate per liter of electrolyte. Evidently, after the plates were tank formed (prior to cell assembly), they were not adequately washed and some residual cuastic was left in the plates. Subsequent drying in a forced air oven, and exposure to the atmosphere while in process, caused a carbonate build-up in the plates, which is the most probable mode in which carbonate was introduced into the cells. To prevent such a recurrence, we have instituted routine analytical tests to determine carbonate and nitrate content in representative positive and negative plate samples. If any of the test results show a residual impurity level which is deemed excessive, the plates are rewashed and retested until satisfactory results are obtained, prior to mechanical assembly.

TABLE IV. - SUMMARY OF CHARACTERIZATION TEST RESULTS

TEST NO.	TEMP. °F	CHARGE RATE	CHARGE TIME	AH INPUT	DISCH. RATE	AMPERE-HOUR OUTPUT CELL NUMBER 1	3	13	21	25
1	70	10 A	15 Hrs	150	10 A	118	111	121	119	112
2	70	10 A	13.5 Hrs	135	25 A	126	127	126	127	127
3	70	10 A	16 Hrs	160	50 A	117	110	116	116	118
4	70	10 A	16 Hrs	160	100A	118	112	119	112	120
5	70	25 A	6 Hrs	150	100A	*	*	*	*	*
6	70	25 A	6 Hrs	150	50 A	122	110	117	110	119
7	70	50 A	145 Min	121	100A	114	105	114	106	115
8	70	50 A	145 Min	121	25 A	122	120	121	121	124
9	70	100A	75 Min	125	100A	119	117	117	116	120
10	70	50A/10A	1.5Hr/12Hrs	195	10 A	138	135	134	135	136
11	70	50 A	2.5 Hrs	125	25 A	120	118	119	120	120
12	70	10 A	13 Hrs	130	25 A	115	115	114	116	117
13	50	50 A	2.5 Hrs	125	25 A	119	118	118	120	120
14	50	10 A	13 Hrs	130	25 A	124	120	121	119	123
15	50	10 A	12 Hrs	120	100A	112	108	110	107	111
16	50	10 A	12.5 Hrs	125	10 A	135	132	131	130	134
17	50	10 A	12 Hrs	120	50 A	122	115	118	113	121
18	50	25 A	5 Hrs	125	50 A	118	114	116	112	117
19	50	100A	70 Min	117	100A	113	110	112	109	113
20	50	25 A	340 Min	142	100A	118	115	117	115	117
21	50	50 A	140 Min	117	100A	116	114	115	112	116
22	90	50 A	2.5 Hrs	125	25 A	121	122	120	124	122
23	90	25 A	6 Hrs	150	100A	116	118	115	115	118
24	90·	25 A	6 Hrs	150	50A	114	116	113	113	116
25	90	50 A	2.5 Hrs	125	100A	109	108	108	102	110
26	90	100A	80 Min	133	100A	119	116	117	112	119
27	90	10 A	16 Hrs	160	50 A	91	88	88	91	93
28	90	10 A	16 Hrs	160	25 A	88	81	83	85	89
29	90	10 A	16 Hrs	160	10 A	106	90	102	101	106
30	90	10 A	16 Hrs	160	100A	86	73	78	67	83
31	90	10 A	16 Hrs	160	100A	80	68	66	58	73
32	90	50 A	2.5 Hrs	125	100A	104	99	100	99	101
33	90	50 A	2.5 Hrs	125	25A	104	104	105	105	105
34	90	10 A	13 Hrs	130	25 A	90	88	83	82	87
35	110	25 A	5 Hrs	125	50 A	68	66	65	57	67
36	110	25 A	5 Hrs	125	100A	59	54	54	55	57
37	110	50 A	2.5 Hrs	125	50 A	90	88	83	85	88
38	110	50 A	2.5 Hrs	125	100A	92	89	88	91	91
39	32	25 A	4.5 Hrs	113	50 A	98	96	96	92	96
40	32	25 A	**	75-106	100A	87	75	74	67	80
41	32	10 A	**	80-102	50 A	102	92	85	85	94
42	32	10 A	**	80-112	100A	103	78	73	73	80
43	70	25 A	5 Hrs	125	100A	101	103	104	104	104
44	70	10 A	13 Hrs	130	100A	114	109	112	113	114

* Low capacity due to inadequate charge

** Ampere-hour inputs to 1.50 V/cell

30

FIGURE 13. CELL VOLTAGE Vs AMPERE-HOUR INPUT AT 70°F
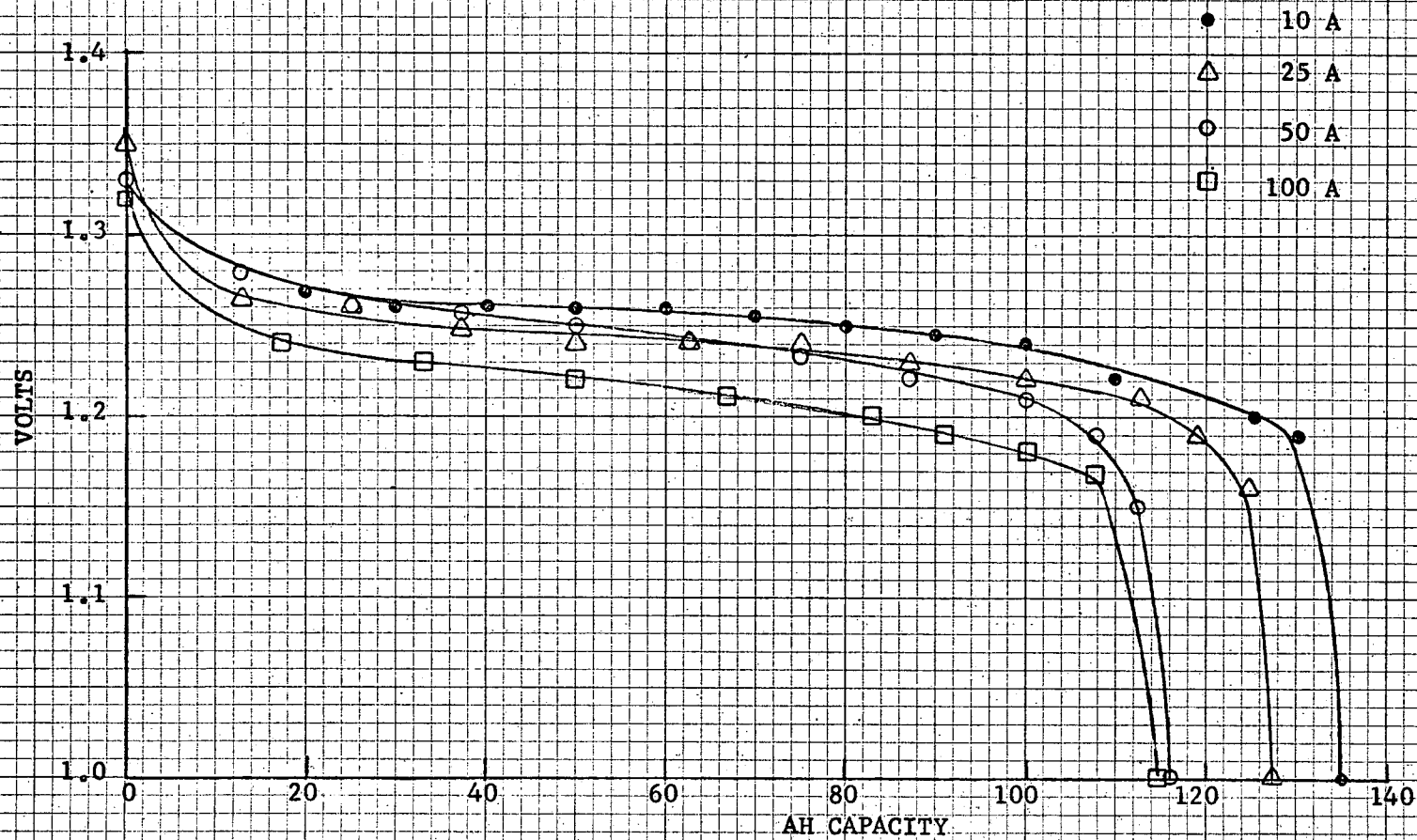10 A, 25 A, 50 A AND 100 A CHARGE RATES
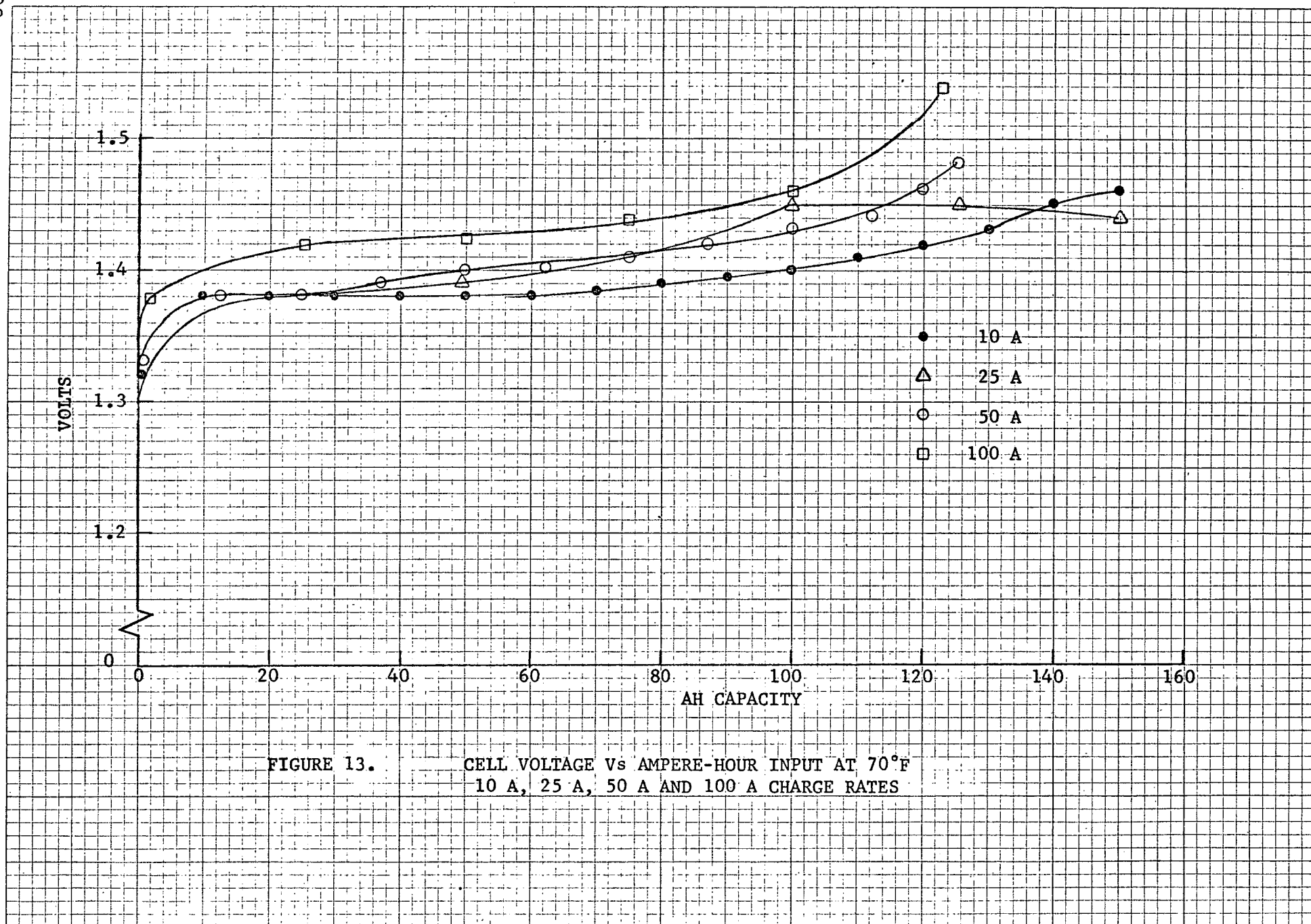
FIGURE 14.   CELL VOLTAGE Vs AMPERE-HOUR OUTPUT AT 70°F
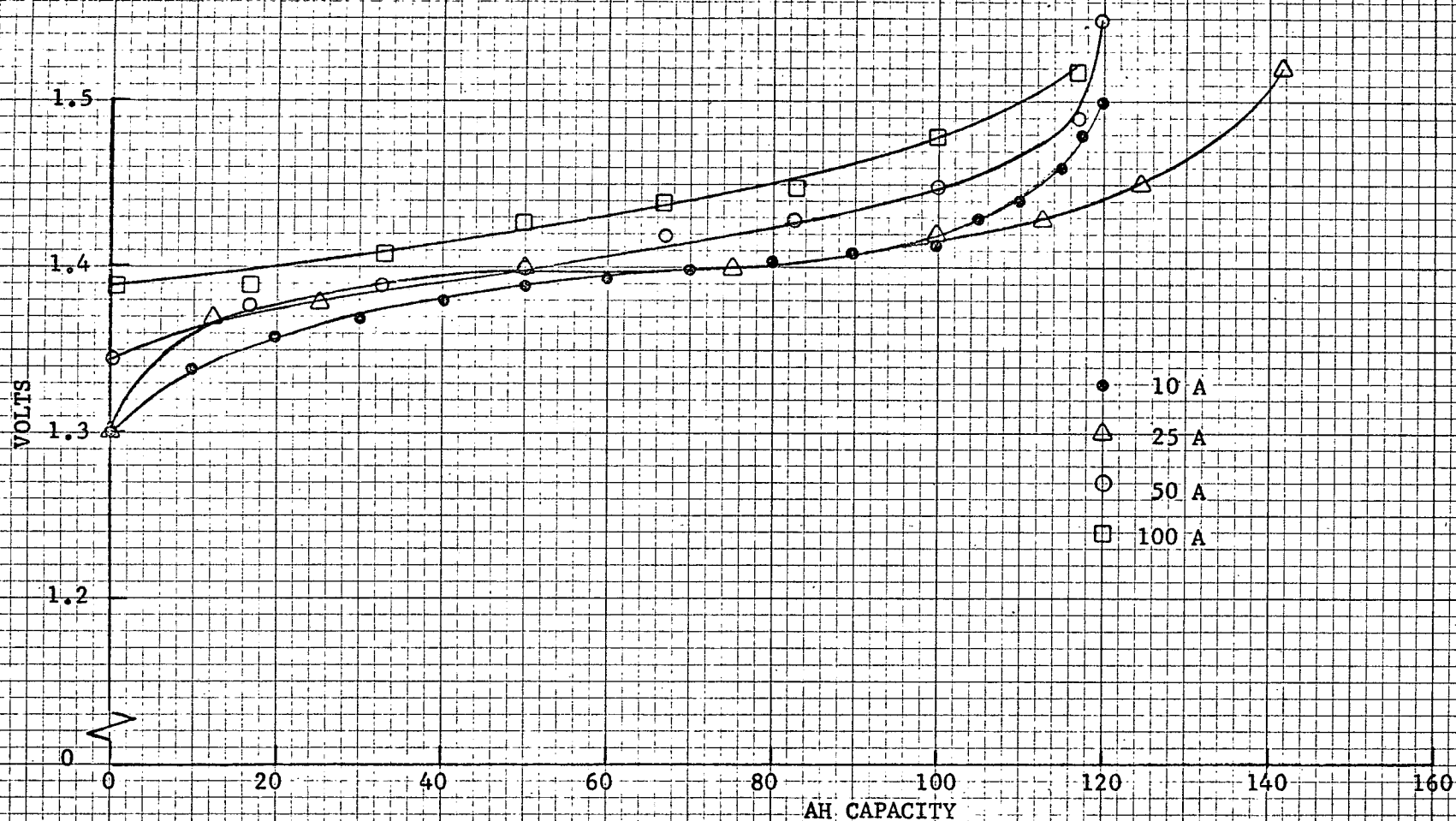10 A, 25 A, 50 A AND 100 A DISCHARGE RATES

FIGURE 15.   CELL VOLTAGE Vs AMPERE-HOUR INPUT AT 50°F
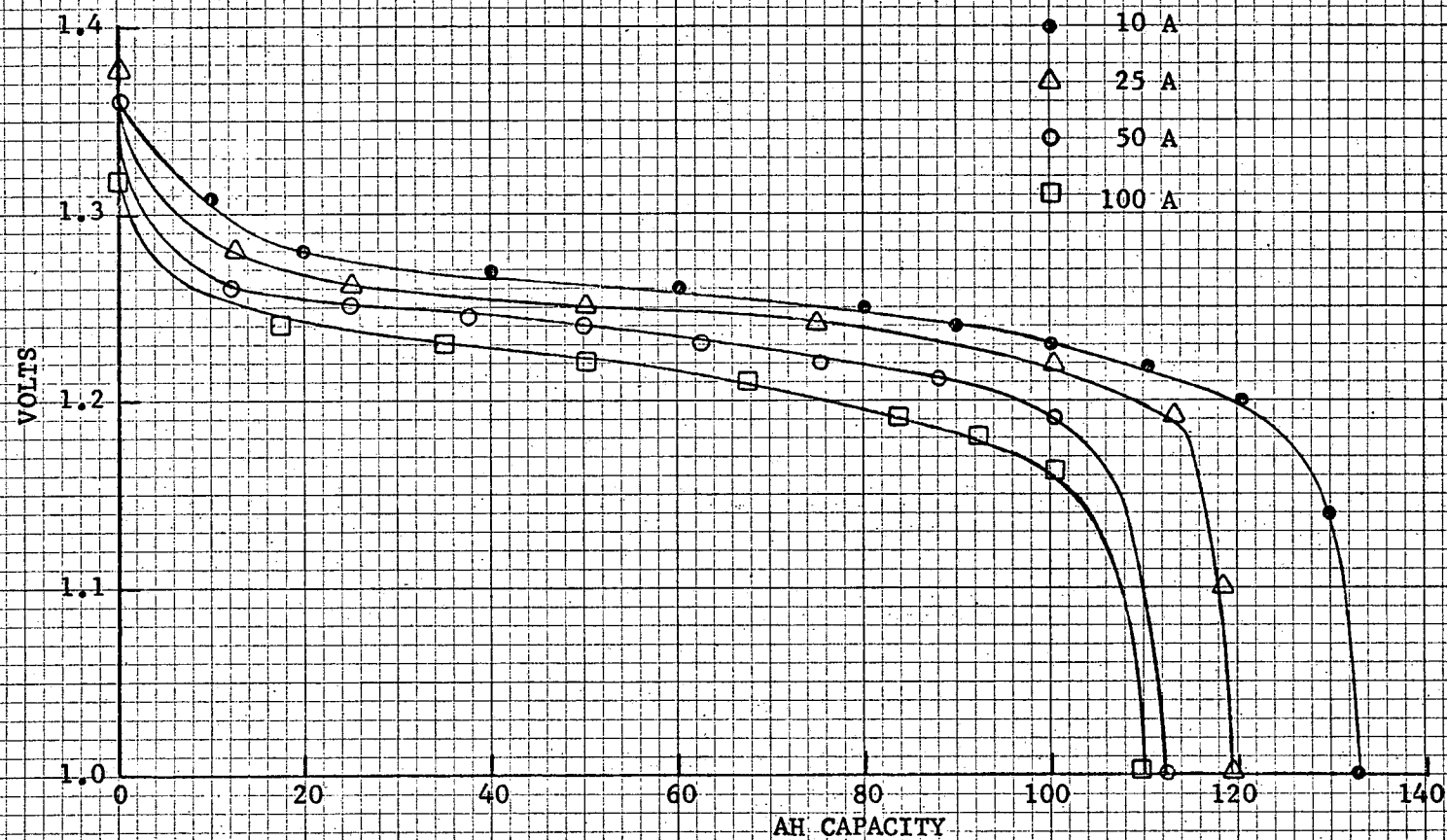10 A, 25 A, 50 A AND 100 A CHARGE RATES

FIGURE 16.   CELL VOLTAGE Vs AMPERE-HOUR OUTPUT AT 50°F

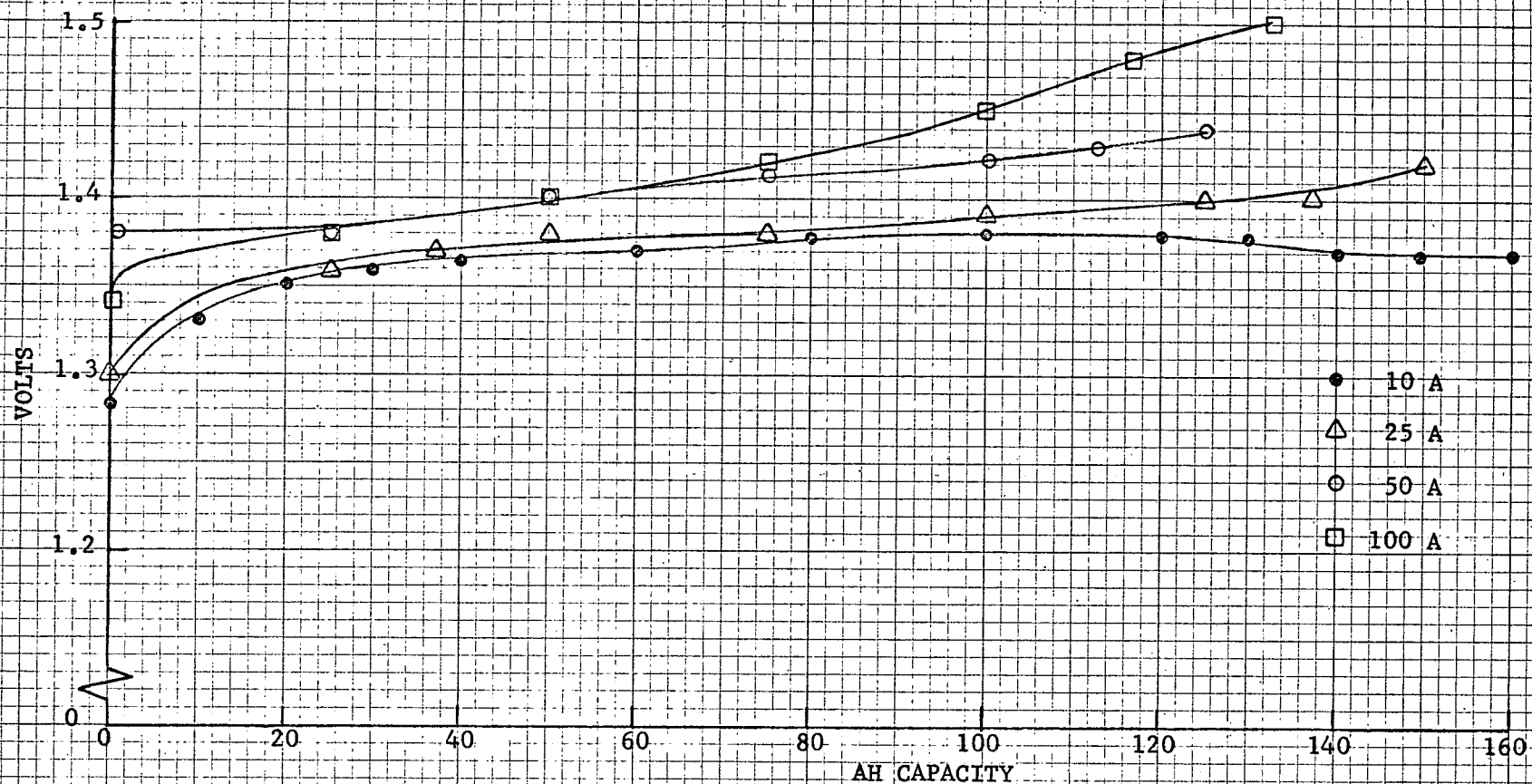10 A, 25 A, 50 A, AND 100 A DISCHARGE RATES

FIGURE 17.   CELL VOLTAGE Vs AMPERE-HOUR INPUT AT 90°F
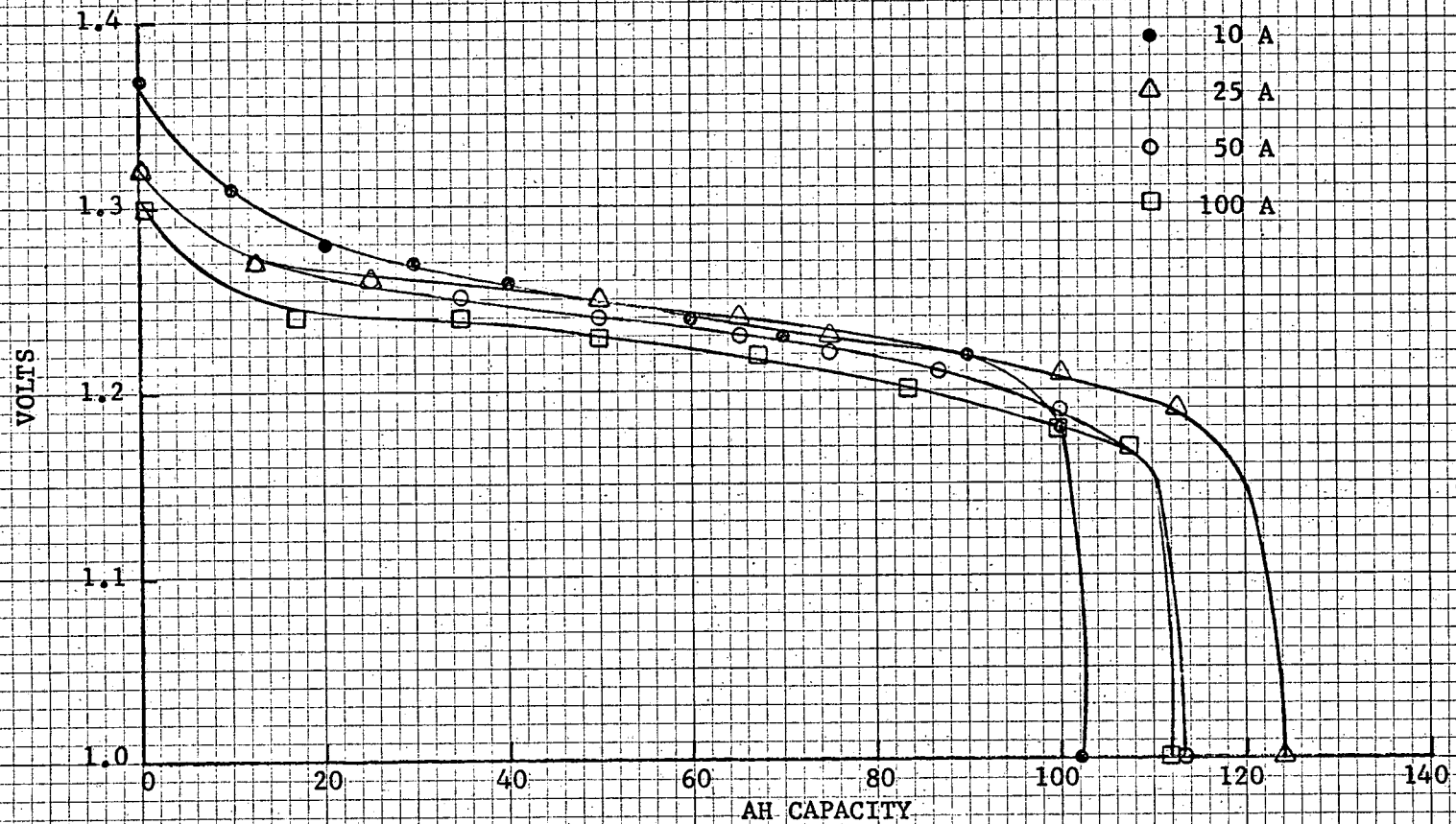
10 A, 25 A, 50 A AND 100 A CHARGE RATES

FIGURE 18. CELL VOLTAGE Vs AMPERE-HOUR OUTPUT AT 90°F
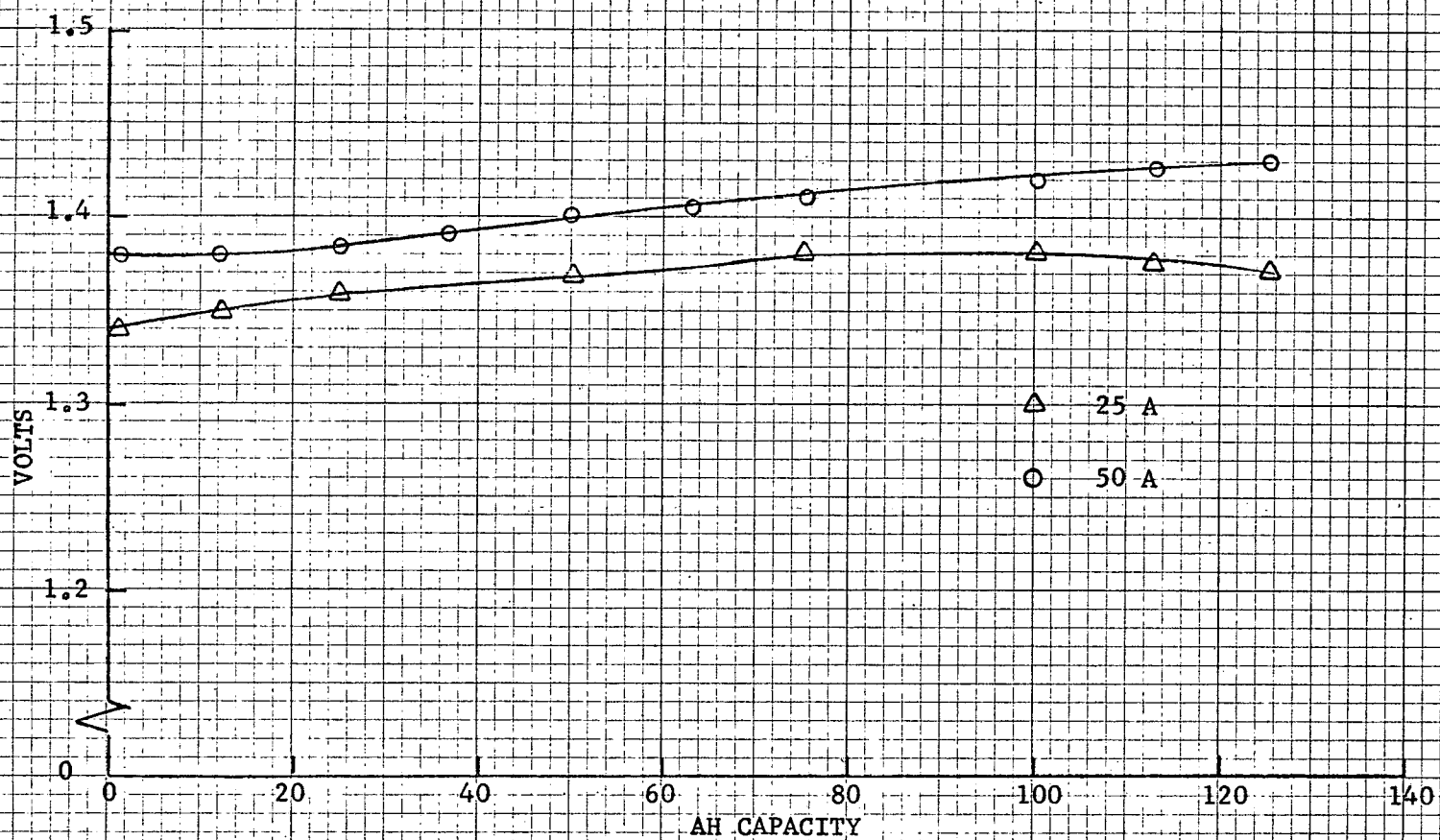10 A, 25 A, 50 A, AND 100 A DISCHARGE
RATES

FIGURE 19.   CELL VOLTAGE Vs AMPERE-HOUR INPUT AT 110°F

25 A AND 50 A CHARGE RATES

FIGURE 20.   CELL VOLTAGE Vs AMPERE-HOUR OUTPUT AT 110°F
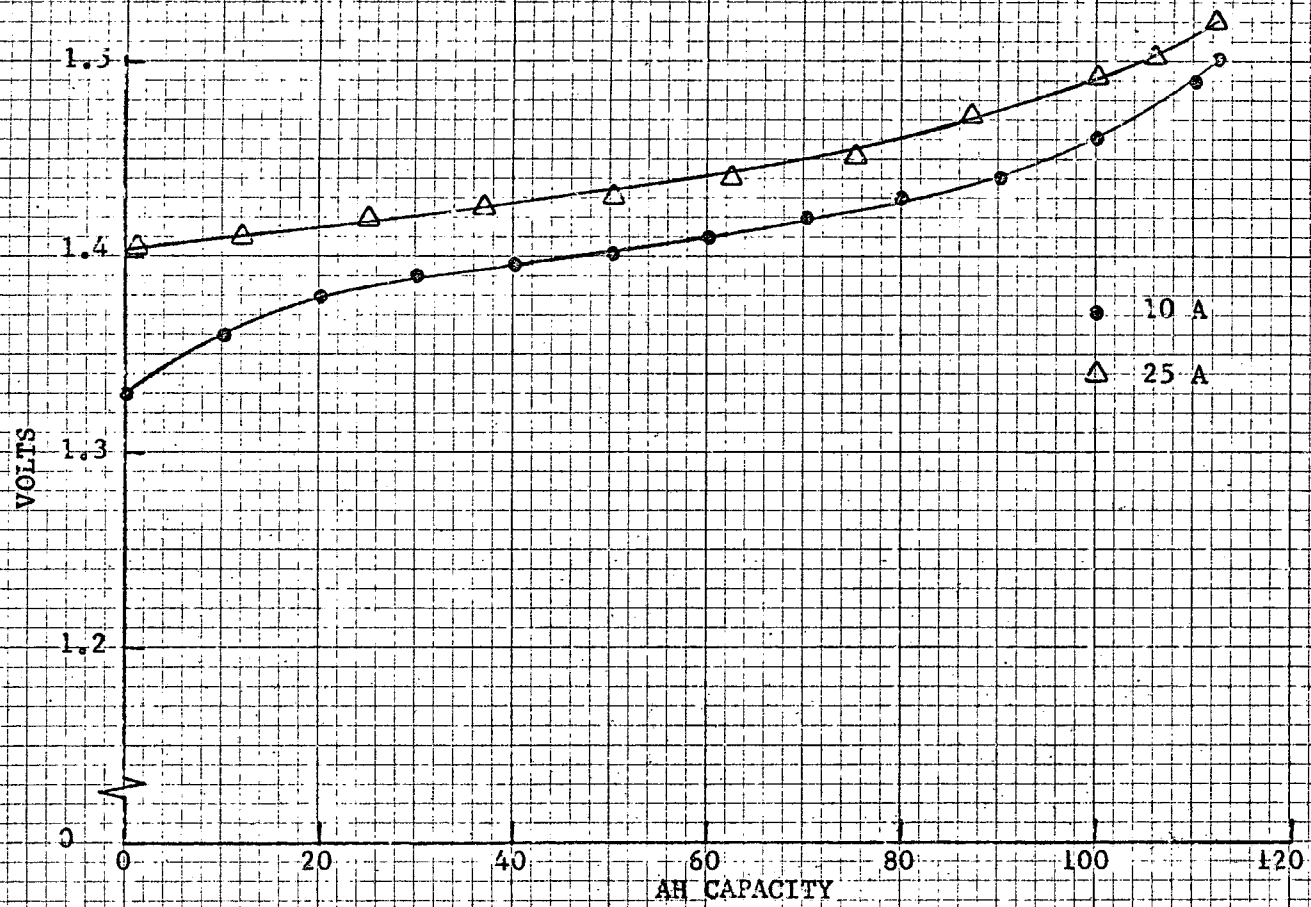50 A AND 100 A DISCHARGE RATES

FIGURE 21.   CELL VOLTAGE Vs AMPERE-HOUR INPUT AT 32°F
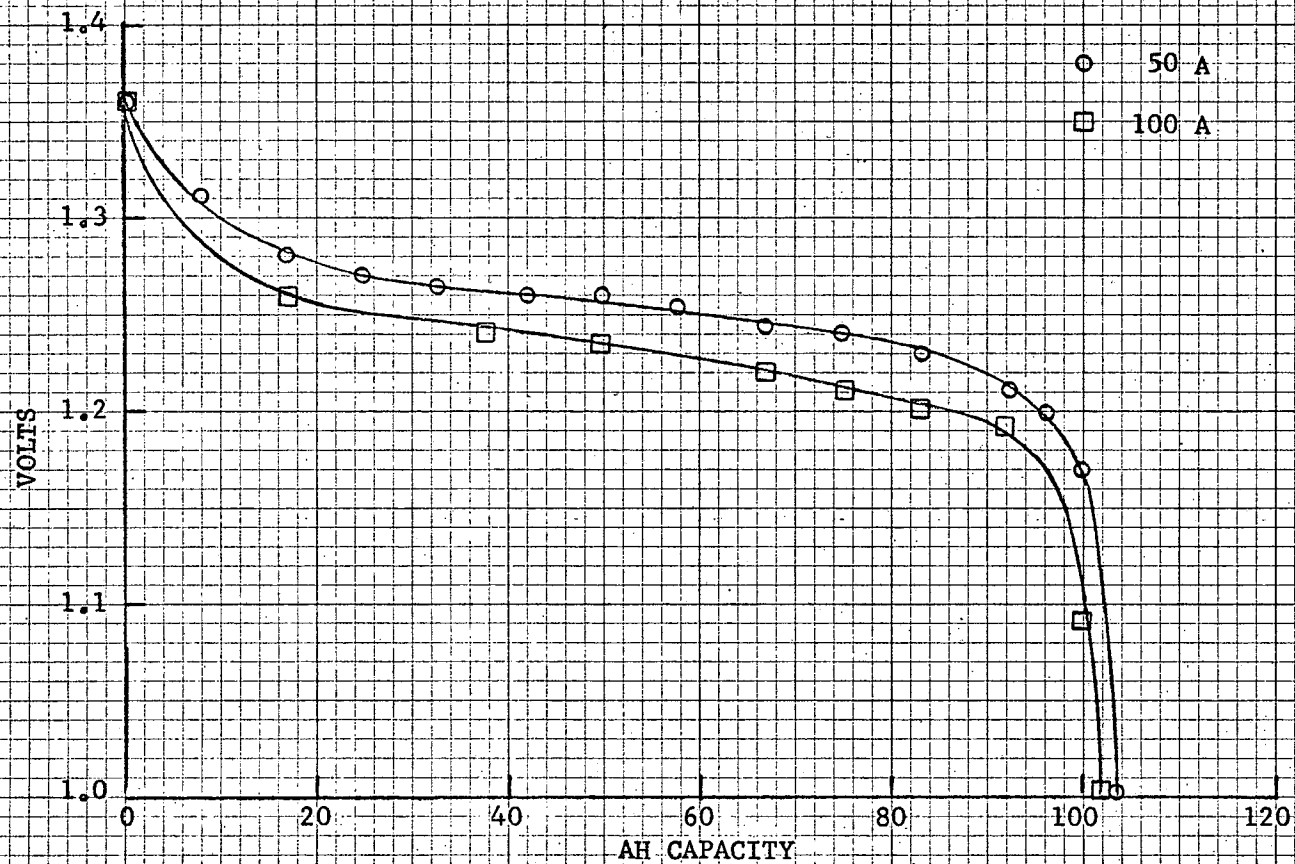10 A AND 25 A CHARGE RATES

FIGURE 22.   CELL VOLTAGE Vs AMPERE-HOUR OUTPUT AT 32°F
50 A AND 100 A DISCHARGE RATES

TABLE V. - CHARGING EFFICIENCY OF 100 AH NICKEL-CADMIUM CELLS

TEST NO.	TEMP. °F	CHARGE RATE	CHARGE TIME	AH INPUT	DISCH. RATE	CHARGING EFFICIENCY CELL NUMBER 1	3	13	21	25
2	70	10 A	13.5 Hrs	135	25 A	0.94	0.94	0.94	0.94	0.94
12	70	10 A	13 Hrs	130	25 A	0.88	0.88	0.88	0.89	0.90
11	70	50 A	2.5 Hrs	125	25 A	0.96	0.95	0.95	0.96	0.96
14	50	10 A	13 Hrs	130	25 A	0.95	0.92	0.93	0.92	0.95
13	50	50 A	2.5 Hrs	125	25 A	0.95	0.95	0.95	0.96	0.96
28	90	10 A	16 Hrs	160	25 A	0.55	0.51	0.52	0.53	0.56
33	90	50 A	2.5 Hrs	125	25 A	0.84	0.84	0.84	0.84	0.84

To confirm our suspicion that the high carbonate content was responsible for the poor electrical performance observed at 32°F, Cell #21 was flushed with 34% KOH solution. The cell was flooded, and after a 24 hour stand at 120°F, drained under vacuum. This procedure was repeated six times, and after the last flush, the electrolyte quantity in the cell was adjusted to the original amount by extracting the excess on a centrifuge. The extracted solution had an assay of 33% KOH and 47 gm K_2CO_3/ℓ.

The cell was retested at room ambient and in a chamber at 32°F with the following results:

TEMP.	CHARGE		AH	DISCHARGE	CAPACITY	DISCHARGE VOLTAGE
	RATE	TIME	INPUT	RATE	TO 1.0V (Ah)	AT MIDPOINT
R.T.	10 A	18 Hr.	180	50 A	133	1.24
R.T.	10 A	18 Hr.	180	50 A	128	1.24
R.T.	10 A	16.5 Hr	165	50 A	122	1.26
32°F	25 A	6 Hr.	150	50 A	122	1.26
32°F	25 A	6 Hr.	150	50 A	121	1.25
R.T.	50 A	2.7 Hr.	135	50 A	122	1.26
32°F	25 A	6 Hr.	150	31 A*	125*	1.26

* Constant load (0.04 ohm) discharge, capacity estimated at 125 Ah.

Cell was shorted with 0.02 ohm resistor for 4 hrs. after each discharge.

Excessive amounts of carbonate in the electrolyte are known to have an adverse effect on low temperature performance, and these test results indicate that the poor electrical performance originally experienced at 32°F was indeed caused by the high carbonate level present in the cells.

CONCLUSIONS

A 100 Ah nickel-cadmium cell of improved design was developed which met, or exceeded, the specified cell requirements. The specific improvements in the cell design are:

1. Lower internal impedance

2. Reduced load sensitivity

3. Improved voltage characteristics and higher usable energy output.

4. Reduced level of waste-heat generation.

RECOMMENDATION

It is recommended that the cells be subjected to cycle-life testing at several test temperatures and to varying depths of discharge to evaluate this cell design.

1.0 EQUIVALENT CIRCUIT FOR CALCULATING RESISTANCE OF TERMINAL ASSEMBLY
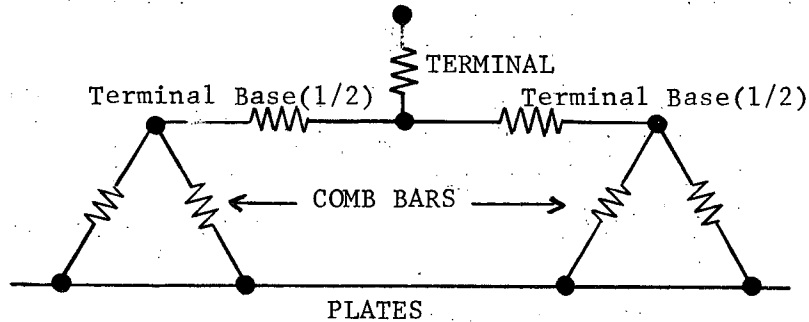
1.1 Terminal

$$\rho = 1.71 \times 10^{-6} \text{ ohm-cm}$$

$$A = 0.1963 \text{ sq. in.} = 1.27 \text{ cm}^2$$

$$L = 0.625 \text{ in} = 1.59 \text{ cm}$$

$$R = \rho \frac{L}{A} = \frac{1.71 \times 10^{-6} \times 1.59}{1.27} = 2.14 \times 10^{-6} \text{ ohms}$$

1.2 Terminal Base

$$\rho = 11.0 \text{ microhm-cm}$$

$$A = 1.12 \times .24 = .267 \text{ in}^2 = 1.72 \text{ cm}^2$$

$$L = 2'' = 5.08 \text{ cm}$$

$$R = \frac{11 \times 10^{-6} \times 5.08}{1.72} = 32.49 \times 10^{-6} \text{ ohms}$$

1.3 Comb

$$\rho = 11.0$$

$$A = 4(1.12 \times .12) = .534 \text{ in}^2 = 3.44 \text{ cm}^2$$

$$L = 1.6'' = 4.06 \text{ cm}$$

$$R = \frac{11.0 \times 10^{-6} \times 4.06}{3.44} = 12.98 \times 10^{-6} \text{ ohms}$$

Total

$$2.14 \times 10^{-6} \text{ ohms}$$

$$32.49 \times 10^{-6} \text{ ohms}$$

$$\underline{12.98 \times 10^{-6} \text{ ohms}}$$

$$47.61 \times 10^{-6} \text{ ohms} \quad - \quad \text{one end of cell}$$

$$\underline{\times 2}$$

$$95.2 \times 10^{-6} \text{ ohms} \quad - \quad \text{both ends of cell}$$

2.0   CONTRIBUTION FROM PLATE SUPPORT

From data in Figure 3

$$R = \frac{E}{I} = \frac{0.0015 \text{ V}}{3.5 \text{ A}} = 4.3 \times 10^{-4} \text{ ohms}$$

Where 0.0015 V was the average IR drop with 3.5 A current flowing. Since there are 15 plates in parallel, the total resistance would be

$$\frac{4.3 \times 10^{-4}}{15} = 29 \times 10^{-6} \text{ ohms}$$

3.0   IMPEDANCE ACROSS SEPARATOR-ELECTROLYTE LAYER

The resistance of the separator-electrolyte layer, 0.204 ohms-sq in, was calculated from experimental measurements $(\Delta E / \Delta I)$ by the method of successive approximations.

The total positive electrode surface area was 1240 sq. in. Consequently, the total impedance of the separator-electrolyte layer was calculated to be

$$\frac{0.204 \text{ ohm-sq.in.}}{1240 \text{ sq. in.}} = 165 \times 10^{-6} \text{ ohms}$$